



**STUDIES ON THE CHARGE TRANSFER
COMPLEXES OF NON-CONVENTIONAL
DONORS AND ACCEPTORS IN
SOLID STATE**

ABSTRACT

THESIS

SUBMITTED FOR THE DEGREE OF

Doctor of Philosophy

IN

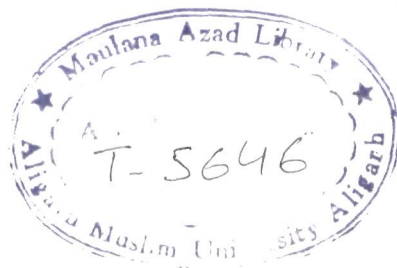
CHEMISTRY

BY

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2000



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ABSTRACT

Molecular interactions are basically all those interactions where no chemical bonds are formed. Extending from hydrogen bonding to proton transfer reactions to charge-transfer complexes or molecular complexes. There is now growing opinion that these complexes are involved on the reaction profiles of all chemical reactions. The present study has been undertaken primarily to get some insight into the understanding of the molecular complexes.

The thesis is divided into five chapters.

The first chapter is with regard to the general introduction to the charge-transfer complexes. Apart from the general survey of the literature on the subject, the emphasis in this chapter is towards the existing theory of the charge-transfer complexes given by Mulliken. The behaviour of these complexes towards various spectroscopic techniques viz, multiple charge-transfer spectra, UV-visible and IR-spectroscopy have also been discussed. The calculation of equilibrium constant with the IR spectroscopy has also been elucidated.

The second chapter comprises the interaction of Diphenylamine with p-Dimethaminobenzaldehyde (p-DAB). The reaction has been studied by capillary technique. We have given a new method for the spot-test, called capillary spot test. In this

chapter the detection of product (complex) was determined in solid-state by solid-state spot-test in the capillary. The thickness of the product in the capillary varies linearly with time. By studies at different temperatures the limit of identification has also been reported.

In the third chapter, kinetic data for the reaction between O-Nitroaniline and p-Dimethylaminebenzaldehyde (p-DAB) in the solid-state are recorded. The experimental data fit best in the equation

$$\zeta^2 = kt$$

Where ζ is the thickness of the coloured boundary, k is a constant, and t is the time. Many tests have been performed to ascertain the diffusion mechanism and nature of the product obtained.

This chapter deals with (the isolation of charge-transfer for various polynitroaromatics-aromatic amine systems). Even though efforts have been made, these bands could not be isolated before. The charge-transfer has been confirmed independently by evaluating association constants.

Nitroaniline has been a centre of controversy in its molecular complexes. Usually it is difficult to distinguish whether

there is a charge-transfer or hydrogen bonding in several of its complexes.

In fourth chapter, convincing evidence have been given that both the interactions π - π and π - π^* (between p-Nitrophenol with p-DAB) are simultaneously involved. This has been established by using IR spectrometry. Also in this chapter detection of product (complex) was determined in solid-state spot-test in the capillary. The rate equation satisfying the result is given by

$$\zeta^2 = 3.125 \log t - 1.8$$

Association constant K evaluated by the method of Foster under the condition $[A]_0 = [D]_0$ with applying this equation.

$$\frac{[A]_0}{A} = \frac{1}{k\epsilon_\lambda} \frac{1}{[D]_0} + \frac{2}{\epsilon_\lambda}$$

Where $[A]_0$ is the initial concentration of acceptor equal to $[D]_0$. A is the absorbance of the complex at λ , k is the association constant and ϵ_λ is the molar absorptivity of the complex at λ .

In the IR spectral studies of several related organometallic compounds, one comes to the conclusion that p-Nitrophenol shows a broad band centred at 1600 cm^{-1} and to nitroasymmetric stretching vibrations. In the complex while the 1500 cm^{-1} band remains without shift, the broad band localized at 1600 cm^{-1} shift to 1610 cm^{-1} . A shift of 10 cm^{-1} shows a weak interactions.

Studied on molecular complexes of organometallic donors and acceptors is of very recent origin. Though alkyl donors have been extensively studied, very few studies have appeared on aryl donors.

Fifth chapter deals with a study on the charge-transfer complex between p-Dimethylaminobenzaldehyde (p-DAB)-3,5-Dinitrobenzoic acid (DNBA) and spectrophotometric method for the determination of the formula of the complex. An interesting feature of this study is that two charge-transfer bands are observed. IR studies confer the molecular complexation in this system. Equilibrium constant has been measured.

A major problem in the evaluation of association constants for molecular complexes by graphical methods based on Benesi-Hildebrand equation is that a separation of terms in $k\varepsilon$ is required which leads to significant donors. Therefore, in the fifth chapter a new equation is proposed for UV-visible region. The equation takes the form:

$$\text{UV-visible:} \quad \frac{1}{[D]_0} = \frac{k\varepsilon[A]_0}{A} - k$$

By using above equations k may be evaluated directly without separation of k ; though evaluation of k require a separation of the terms. However, k is usually the desired parameters and since k is comparatively very large, the errors involved in the equation will be small.

It is seen that though in all cases studied, the λ_{\max} remains the same, and k and ϵ_{\max} change dramatically. k increases from 25.0 in pure acetone to 625.0 in 60:40 mixture of acetone/water. λ_{\max} does not show any particular trend with k and neither is this expected. The almost abnormally large increase in k as the water content increases shows that electrostatic effects predominate. Further when in one particular case (80:20, Acetone/water mixture) the measurements for k were carried out away from λ_{\max} (370 nm) i.e. at 420nm a large wavelength dependence in k was found (Table 1). This observation confirms the role of electrostatic contributions.

Table-1

K and λ_{\max} for the 3,5-Dinitrobenzoicacid and p-Dimethylaminobenzaldehyde charge-transfer system in pure Acetone and mixed aqueous solvents of Acetone.

Solvent	$\lambda_{\max}(\text{nm})$	K	ϵ
Acetone	420	25.0	1.33
Ace/H ₂ O (80:20)	420	30	66.6
Ace/H ₂ O (70:30)	420	290	11.5
Ace/H ₂ O (60:40)	420	625	40



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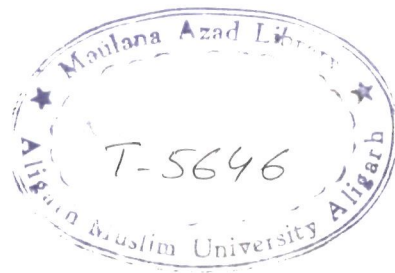
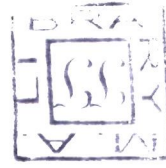
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CERTIFICATE

It is certified that the thesis entitled, "*Studies On the Charge-Transfer Complexes of Non-Conventional Donors and Acceptors in Solid-State*" is the original work carried out done by *Mr. Ahmad Naeem* under my supervision and is suitable for consideration of award of *Ph.D.* degree.

(Dr. Afaq Ahmad)
Supervisor

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A handwritten signature in cursive script, reading 'Ahmad Naeem', with a horizontal line drawn underneath the name.

(Ahmad Naeem)

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INTRODUCTION

Molecular association is a blanket term which includes all those interactions where no chemical bonds are formed. They extend from hydrogen bonding to proton transfer reactions and include the most important of this family of interactions namely charge-transfer complexes or molecular complexes, including solvent polarity scales based on them. These complexes are becoming increasingly important in all fields of human endeavour from physics and chemistry and biology to medicines. Currently there is an opinion among some scientists that these complexes are involved somewhere or the other on the reaction profile of all chemical reactions. These are a special case of molecular association and have been most widely investigated.

The Theory of Charge-Transfer Complexes:

It has been known for a long time that hydrocarbons such as naphthalene react with picric acid to form a coloured substance. The nature of these coloured substances has only been recently understood. Briegleb^{1,2} suggested that the hydrocarbon-nitro compound adducts were the result of the electrostatic attraction between the localized dipoles of the nitro groups and the induced dipoles in the hydrocarbons. This theory could explain the bonding energy of a few kilocalories per mole which had been observed. However, the formation of colour could not be explained by this theory. Pauling³ suggested that when a hydrocarbon molecule is close

to picric acid (at a distance of a 3.5\AA) and also parallel to it then the dielectric constant of the environment of the picric acid molecule is affected. This effect results in greater optical absorption. The distance between the component molecules in a complex was shown by crystallographic measurements to be only slightly less than the Van der Waal's distance.⁴⁻⁷ This observation finally removed the possibility that any sort of normal covalent bonding could be responsible for these complexes. On theoretical considerations too, the instant equilibrium in solution disfavors covalent bonding.

In 1949 Benesi and Hildebrand⁸ reported that solutions containing an aromatic hydrocarbon and iodine had an electronic absorption band not present in either component separately. In 1950 Mulliken⁹ suggested that complex formation occurs through an intermolecular charge-transfer transition. The detailed theory was put forward by him in 1952.^{10,11} As a result of Mulliken's theory there has been a great stimulus to the developments in the study of the charge-transfer (CT) complexes. A brief outline of his theory is presented here.

Mulliken's Theory:

Mulliken defines a molecular complex between two molecules as an association somewhat stronger than ordinary. Van der Waal's association of definite stoichiometry (1:1 for most cases). The partners are very often already closed-shell (Saturated Valence)

electronic structure. In loose complexes the identities of the original molecules are to a large extent preserved. The tendency to form complexes occurs when one partner is an electron acceptor and the other is an electron donor. We abbreviate the term donor-acceptor complex to include all such associations and use D for an electron donor and A for electron acceptor. Most studies of complexes thus far have been made in solution, in solvent that are as inert as possible. We may, therefore, assume that the London dispersion interactions which are important between D and A in the vapour state, are very approximately cancelled by losses of solute-solvent dispersion force attractions when complex is formed from free donor and acceptor in solution. Roughly one donor- solvent plus one acceptor- solvent contact is replaced by one donor-acceptor and one solvent-solvent contact. The theory of donor-acceptor complexes and their spectra as presented by Mulliken is a vapour-state theory, except for the omission of the London dispersion attraction terms. This theory after small correction for solvation energies is essentially valid for solutions in inert solvents. The few studies that have been made in vapour-state complexes are in general, in agreement with this theory but they show some puzzling features.

The new bond formed by Benesi and Hildebrand is in the ultra-violet region for a solution of benzene and iodine dissolved in n-heptane. Similar bonds also occur in the visible region for many

other complexes. This demonstrate that a solution of tetracyanoethylene (TCNE) in methylene dichloride may be added to a series of aromatic hydrocarbons dissolved in methylene dichloride, benzene gives a yellow solution, xylene an orange, durene a deep red and hexamethyl benzene a deep purple. The π -electron molecules, ethylene and benzene can act either as weak donors or weak acceptors. Other things being equal; donor ability increases with decreasing ionization potential (I^D); the acceptor ability with increasing electron affinity (E^A). Among aromatic hydrocarbons I^D decreases and E^A increases with increasing size; graphite with $I^D = E^A$ is the extreme example and is in fact both a good acceptor and a good donor. Starting with any unsaturated or aromatic hydrocarbon, either its donor or its acceptor capability can be strengthened by the introduction of suitable substituent groups. The weak donor properties of benzene are fortified by adding more and more electron-releasing methyl groups greatly fortified the acceptor capability of benzene. The two kinds of molecular complexes discussed above provide examples of n.v. (strong) and π - π^* (weak) complexes. The common types of donors and acceptors are listed in Table(1).

Table - 1

Donor Type	Example	Dative electron ^a from	Acceptor Type	Example	Dative electron goes to
n	:NR ₃	Non-bonding lone pair	V	BCl ₃	Vacant orbital
b ^π	Benzene	Bonding π-orbital	a ^π	TCNE	Antibonding π-orbital
			a ^σ	I ₂ , HQ ^b	Antibonding σ-orbital

- a. "Dative electron" refers to the electron transferred from donor to acceptor.
- b. Molecules such as phenol, water, and other molecules that give hydrogen bonding.

G.N. Lewis¹² explained co-ordination compounds or dative compounds (e.g., $R_3N:BCl_3$ which can also be considered essentially as an stable molecular complex) in terms of a structure with sharing of the electron lone pair of the nitrogen atom as well as the B atom are surrounded by a complete octet of outer-shell electrons. This sharing can be expressed in quantum language by an approximate wave function ψ that is a combination of two resonance structure (D here is R_3N , A is BCl_3):

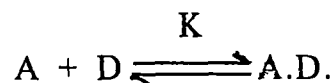
$$\psi_N(AD) \simeq a \underset{\text{no-bond}}{\psi_0(A,D)} + b \underset{\text{dative}}{\psi_0(A^- - D^+)} \quad (1)$$

The dative structure corresponds to an ionic plus a covalent bond and has been called sometimes as semipolar double bond. The interpretation of the N-B dative bond in the complex as given by equation (1) is analogous to the approximate ionic covalent resonance interpretation of the chemical bond in HCl:

$$\psi_{(HCl)} \simeq a \underset{\text{ionic}}{\psi_0(H^+, Cl^-)} + b \underset{\text{covalent}}{\psi_1(H - Cl)} \quad (2)$$

In both examples $b \gg a$. The inclusion of the no-bond structure in equation (1) is given more importance than that of the ionic structure in equation(2).

Complexes are classified as strong or weak depending on whether the energy of formation and the equilibrium constant (K) are large or small. Increasingly strong donors and/or acceptors form increasingly stable complexes.



Equation(1) shows that the complex is stabilized by resonance between ψ_0 and ψ_1 . The forces involved being called charge-transfer (CT) forces. However, classical electrostatic forces (including induction forces) also contribute to the stability of the complexes and may even be of predominant importance for the stability of the most hydrogen bonded complexes and of the weaker of the complexes of the $b.\pi - a.\sigma$ and the benzene-iodine ($b.\pi - a.\sigma$) type.¹³

In terms of the resonance structure description of (1) the structure of the ground state of any 1:1 complex is

$$\psi_N = a\psi_0 (A,D) + b\psi_1 (A^- - D^+)$$

This function is normalized as follows:

$$\int \psi_N \psi_N d\tau = \int a^2 \psi_0^2 d\tau + \int b^2 \psi_1^2 d\tau + \int 2ab \psi_0 \psi_1 d\tau \quad (3)$$

Since ψ_N, ψ_0 and ψ_1 are all normalized hence:

$$\int \psi_N^2 d\tau = 1, \int \psi_0^2 d\tau = 1 \text{ and } \int \psi_1^2 d\tau = 1$$

Substituting these values in equation (3) we obtain

$$a^2 + 2ab \int \psi_0 \psi_1 d\tau + b^2 = 1 \quad (4)$$

$\int \psi_0 \psi_1 d\tau$ is called the overlap integral and is represented by S_{01} with the integration carried over all space. If the complex is loose S_{01} is small and

$$a^2 + b^2 \simeq 1 \quad (5)$$

Here, b^2 approximately measures the weight of the dative structure or the fraction of an electron transferred from the donor to the acceptor in the ground state. The term $2ab\psi_1$ can easily be as large as b^2 or larger. Half of this term can reasonably be assigned to the donor and half to the acceptor so that the fractions F_0 and F_1 in the no-band and dative structure are:

$$F_0 = a^2 + ab\psi_1, F_1 = b^2 + ab\psi_1 \quad (6)$$

In loose complexes between closed -shell donors and acceptors $b^2 \ll a^2$. For benzene, I_2 , I^2 is perhaps 0.06 or less; for pyridine, I_2 , b^2 is approximately 0.2; for trimethylamine, I_2 , b^2 may be 0.4.

If the ground state structure of the complex (weak or strong) is given by ψ_N then according to quantum theory principles, there must be an excited state ψ_E where ψ_E refers to the CT state. ψ_E is given by

$$\psi_E (AD) = a^* \psi_1 (A^- - D^+) - b^* \psi_0 (A, D) \quad (7)$$

The coefficient a^* and b^* are determined by the quantum theory requirement that the excited state wave function be orthogonal to the ground state function i.e. $\int \psi_N \psi_E d\tau = 0$. The excited state function ψ_E is normalized as follows:

$$\int \psi_E^2 d\tau = a^{*2} + b^{*2} - 2a^*b^*S_{01} = 1 \quad (8)$$

This makes $a^* \simeq a$ and $b^* \simeq b$. If S_{01} were zero, $a=a^*$ and $b=b^*$ would be true exactly.

For loose molecular complexes the ground state is mostly no-bond that is, $a^2 \gg b^2$. According to the orthogonality requirements the excited state is mostly dative i.e. $a^{*2} \gg b^{*2}$. The excitation of an electron from ψ_N to ψ_E essentially amounts to the transfer of an electron from D to A. The theory further shows that spectroscopic absorption from ψ_N to ψ_E should occur with generally high intensity.

Complexes have been studied mostly in solution but some studies have been made in solids¹⁴⁻²⁶ and in the case of (non-bonded vacant orbital) n.v. compounds and also recently of a few complexes of weaker types in the vapour state.²⁷ Complexes in solids even when 1:1 stoichiometry do not always occur in the form of pairwise units. Studies in the vapour state are difficult because K is small and interference of overlapping spectra of the uncomplexed components is often severe. These difficulties are also found for solution studies but they are less troublesome because K is larger. The complete absorption spectrum of a complex consists of absorption due to the following:

- (1) Locally excited states (States of A or of D, more or less but usually not greatly modified in the complex).

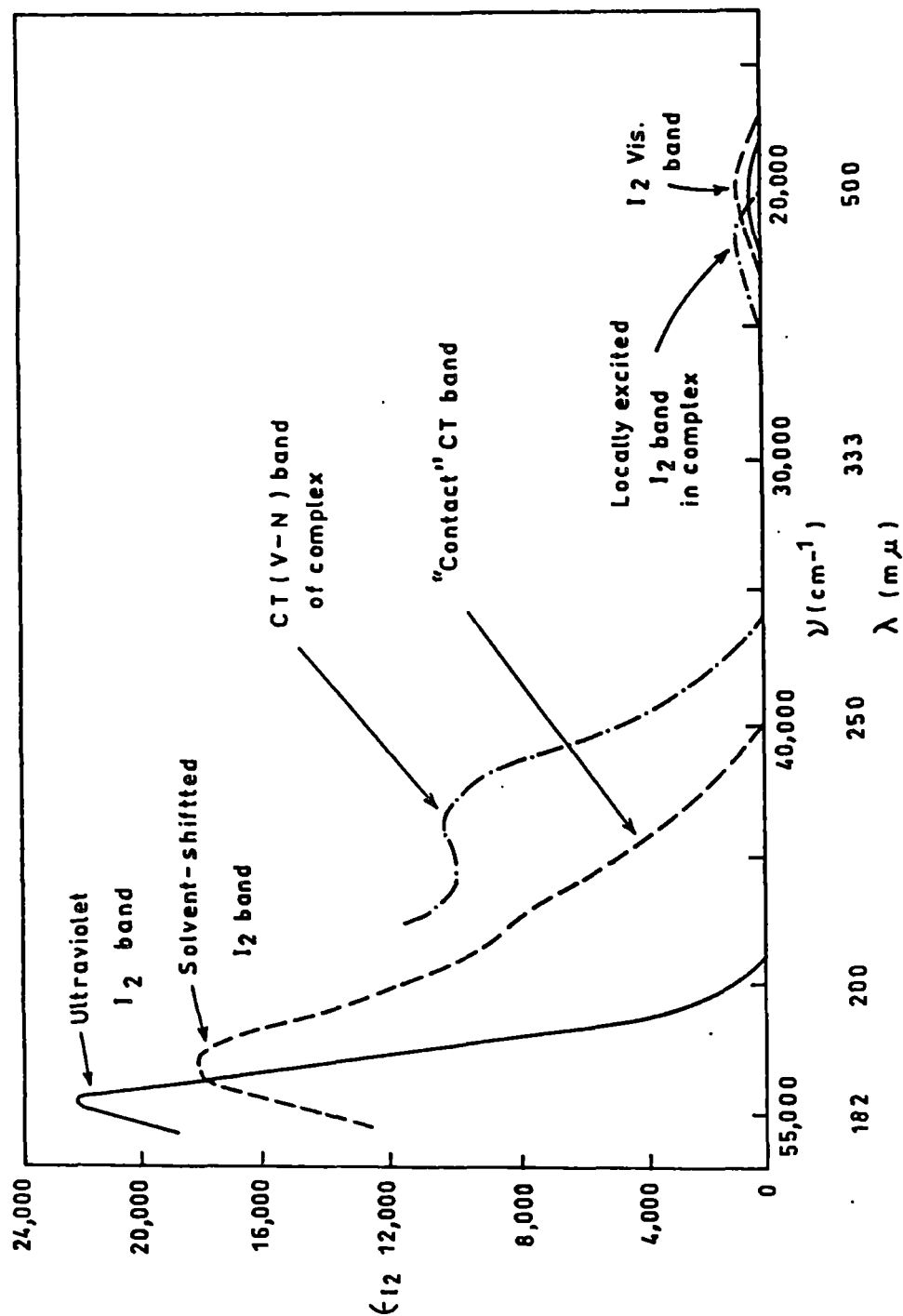


Fig. 1.1: The apparent molar absorptivity of I_2 vapor and of I_2 and EtOH. I_2 in n-heptane, Here I_2 is for I_2 vapor, I_2 in n-heptane, and I_2 in n-heptane with 3.4 M ethyl alcohol.

- (2) CT States [ψ_E , as in eqn. (7) and other CT states involving excited dative structures, for example $\psi_{(D^{+*}-A^-)}$, $\psi_{(D^+-A^{*-})}$].

Figure 1.1 shows the change that occurs in the spectrum of iodine when it dissolves in n-heptane and then when ethanol is added (Ethanol is transparent upto 220 nm).

The maxima of the $C_2H_5OH.I_2$ CT band is marked in the figure (1.1), and the position of the shifted visible absorption band of I_2 in the complex (a transition to a locally excited state) is also indicated. The contact CT band appears as a long wavelength shoulder on the ultraviolet iodine band when I_2 is dissolved in heptane. It is felt by some authors that the importance of CT forces in stabilizing the ground state of such complexes has been exaggerated.

Dewar's Theory:

Mulliken's theory is a valence bond approximation in which the complex formed by a donor D and an acceptor A is represented as a resonance hybrid of the uncharged aggregate (a) and the ionic structure (b) formed it by transfer of an electron from D to A. The appearance of a new band in the spectrum of such a complex is ascribed to a transition from the ground state which is mostly (a) mixed with a little (b) to an excited state which is mostly (b) mixed with little (a). This transition is of CT type and the complexes have accordingly termed CT complexes.

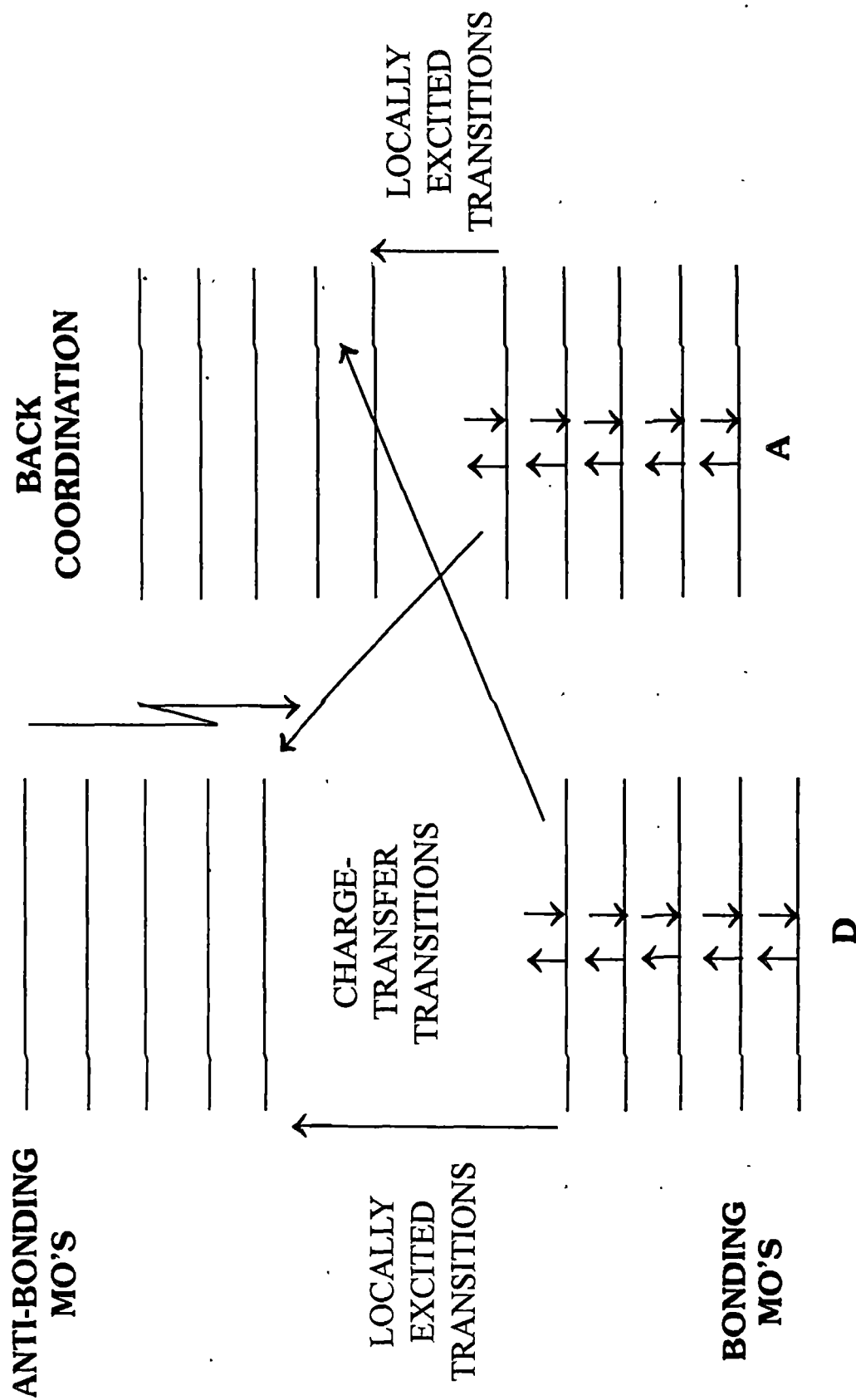


Fig.1.2 Orbital energies and transitions in a molecular complex formed by a donor D and acceptor A.



This problem has been approached in terms of molecular orbital treatment by Dewar and Leply.²⁸ The essential features of this treatment are presented below.

The complex DA is represented as a π – Complex formed by the interactions of the π – orbitals of D and A. As the interaction is small it may be treated by the perturbation theory.²⁹ Consider the orbitals of D and A (Fig. 1.2). Interactions between the filled bonding orbitals of D and A lead to no change in their total energy and there is no net transfer of charge between D and A. Interactions of the filled orbitals of D with the empty antibonding orbitals of A with the empty orbitals of D also lead to stabilization with a net charge-transfer in the opposite direction. These interactions are inversely proportional to the difference in energy between the interacting orbitals. In complexes of this kind one component is normally a molecule of donor type (i.e. with filled orbitals of relatively high energy); the other an acceptor (i.e. with empty orbitals of relatively low energy; the main interaction is therefore between the filled orbitals of the donor and the empty orbitals of the acceptor, as indicated in figure 1.2; this leads to a net transfer of negative charge from the donor D to the acceptor A.

The heats of formation of complexes of this kind are at least an order of magnitude less than their lowest transition energies; this suggests that the changes in energy of the orbitals in forming the complex are small compared with the spacing between the filled (bonding) and empty (antibonding) orbitals. The energies of the orbitals in the complex should, therefore, be little different from those in the separate components. All the possible transitions observed in D and A should, therefore, appear in the spectrum of DA, and this is commonly the case. Transitions of this type are described as locally excited.³⁰ There should also be CT transitions of electrons from a filled orbital of D into an empty orbital of A. Figure 1.2 indicates that transitions of the former kind may occur at lower energies than the locally excited transitions and so lead to the appearance of new absorption bands at lower frequencies. This explains the new bands commonly observed in the spectra of such complexes which are responsible for their colour.

This treatment leads to conclusions similar to those given by the valence bond approach, but it seems preferable for two reasons. First there are cases when more than one new CT band appears in the complex DA; this can be explained in terms of the molecular orbital approach as there should be bands corresponding to transitions between any of the occupied orbitals of D and empty

orbitals of A. Secondly the term "charge-transfer complex" is misleading in that very little charge is transferred in the ground states of such complexes and in that an appreciable part of their stability may be due to back coordination involving interactions between the filled orbitals of the acceptor and the empty orbitals of the donor. The term " π - complex" seems preferable for compounds of this type. If the interactions between donor and acceptor are small, the transition energy ΔE_0 for the first CT band should be either treatment be given by

$$\Delta E_0 = I^D - E^A + \text{Constant} \quad (9)$$

where I^D is the ionization potential of D and E^A is the electron affinity of A. If then the acceptor is kept constant, ΔE_0 should vary linearly with the ionization potential of the donor, this relation has been observed in a number of cases.³¹ In the molecular orbital approach the equation (9) is replaced by the more general equation

$$\Delta E_{ij} = D_i - A_j + \text{Constant} \quad (10)$$

where ΔE_{ij} is the transition energy for the CT band involving the field orbital i of D (energy D_i) and the empty orbital j of A (energy j_A). This is equivalent to equation (9) in the case of first CT band, for the ionization potential of the donor should be equal to the energy of its highest occupied molecular orbital. If equation (10) is valid the energies of the CT transitions should be predictable from simple

molecular orbital theory. Thus the energies of the first CT transitions of a variety of donors with a given acceptor should be a linear function of the energies of the highest occupied orbitals of the donors.

Multiple Charge-transfer Spectra:

We can see from table 2 that the intensity of CT spectra of the iodine-benzene complex is very large and that both the K value and the value of $-\Delta H$ increases proportionately with increasing size of electron donor hydrocarbons. However, the intensity of the CT spectra is inversely proportional with increasing donor size. In particular, CT spectral intensity of the anthraceneiodine complex seems to be weaker than that expected from the assumption that the CT spectra may borrow much of their intensity from strong absorption bands of the donor itself. This assumption is valid because these catacondensed hydrocarbons have several lower excited states allowed strongly from the selection rule. In connection with this problem Murrell³² proposed the following discussion. Generally the MO's of aromatic hydrocarbons spread over the whole molecule so that the overlap between the electron donor orbital and the accepting (σ , μ of the I_2 molecule) orbital becomes smaller for large hydrocarbons than for smaller ones. As a result, the CT intensity of the iodine complexes with large hydrocarbons results in a weaker intensity compared with that of the complexes with small size

Table-2
SPECTROSCOPIC AND THERMODYNAMIC DATA OF IONIC COMPLEXES
WITH SOME AROMATIC HYDROCARBONS

Donor	K_C (Temp.) (Solve)	ϵ_{CT} (λ_{max} CT) (Solve)	ΔH (Solv) ₋₁ K cal mole
Benzene	0.15 (25 ⁰ C) ^a CCl ₄	16.400 (292 mμ) (CCl ₄) ^a	-1.3 (Hexane) ^b (CCl ₄) ^c
Naphthalene	0.25 (25 ⁰ C) ^a CCl ₄	7.150 (360 mμ) (hexane) ^b	-1.8 (Hexane) ^b
Phenanthrene	0.45 (23 ⁰ C) ^d CCl ₄	7,100 (364 mμ) (CCl ₄) ^d	--
Anthracene	3.0 (23 ⁰ C) ^d CH ₂ Cl ₂ , CCl ₄	~550 at 430 mμ (430 mμ) (CCl ₄) ^d	-1.61 (CCl ₄) ^d

a. L.J. Andrews and R.M. Keefer, J. Am. Chem. Soc., **74**, 4500 (1952).

b. J.A.A. Ketelaar, J. Phys. Rad., **15**, 197 (1954).

c. R.M. Keefer and L.J. Andrews, J. Am. Chem. Soc., **77**, 2164 (1955).

d. J. Peters and W.B. Person, J. Am. Chem. Soc., **86**, 10 (1964).

hydrocarbons. At the same time the stability of the complexes should decrease with increasing donor size of hydrocarbons as CT theory suggests. Actually, however, K and $-\Delta H$ value turn out to be larger with increasing size of hydrocarbons, i.e. complexes becomes stable, as Table 2 shows. The main reason for these results may be as follows:

When hydrocarbons increase in size there appear many MO's whose energies are not so well separated from one another. Hence it is possible that the charge-transfer is also brought about from deeper MO's as well as the highest occupied MO of hydrocarbons. Thus these CT states can interact with the ground non-bonding state, resulting in greater stabilization of the ground state. As a net result the complex becomes more stable as the ring size of the hydrocarbon becomes larger. The CT bands caused by the charge-transfer from deep donor orbitals will be hidden under the absorption bands caused by the donors or acceptor themselves.

Multiple CT bands, especially two CT bands, have been reported by many workers for various kinds of molecular complexes. A typical example is shown in figure 1.3³³.

U.V. Visible Spectra:

In general a complex formed between an electron donor and an electron acceptor still retains the absorptions of the components modified to a greater or lesser extent, together with one or

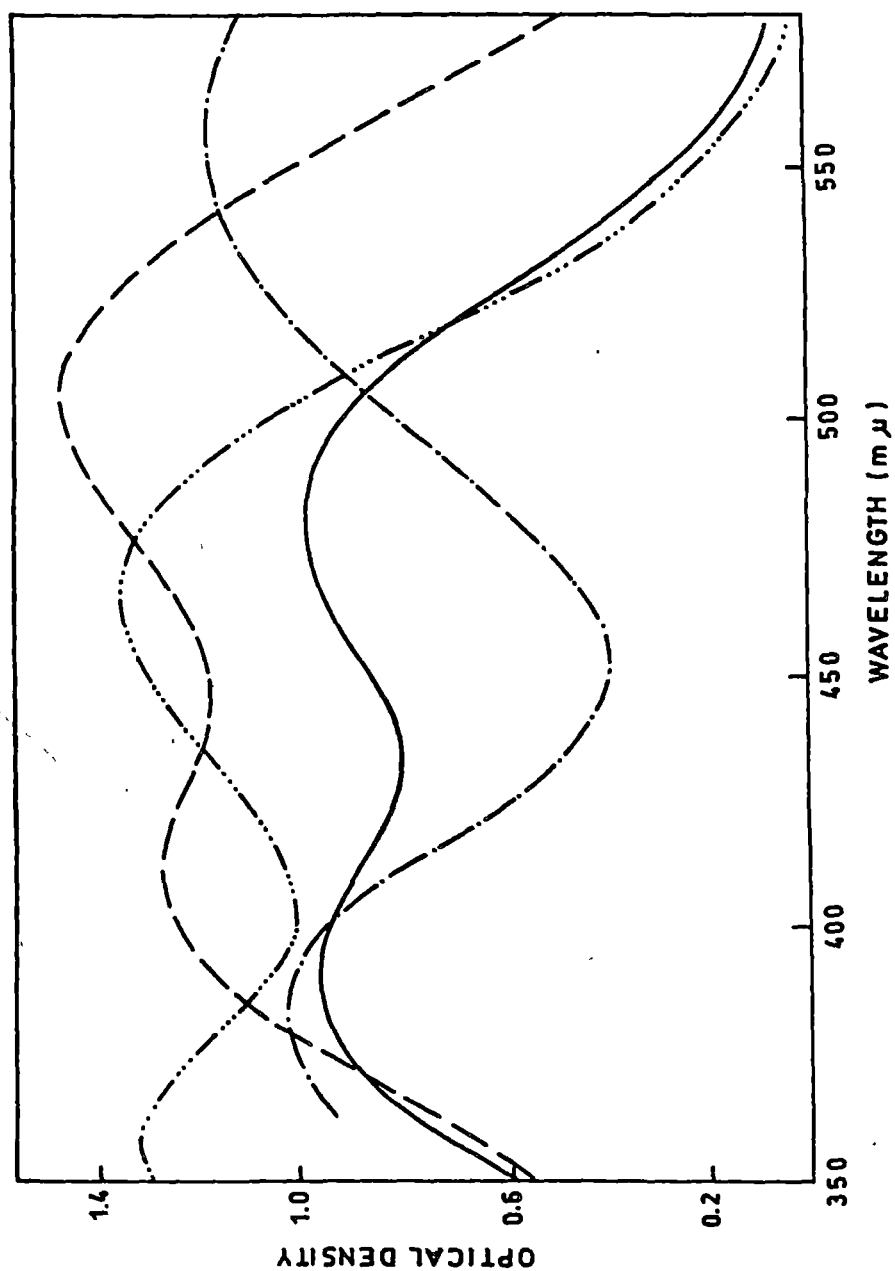


Fig.1.1.3: Two CT absorption spectra observed on the chloranil-substituted naphthalene π - π complexes in CCl_4 : — α -methyl-naphthalene, --- α -chloronaphthalene, -.- α -methylnaphthalene, .-. α -methyxnaphthalene. [Reproduced from A. Kuboyama, J. Chem. Soc. Japan, 83, 376 (1962)].

absorption bands characteristic of the complex as a whole. The recognition of this fact by Brackman³⁴ was important historically because it led to the realization that the absorption is the result of an intermolecular charge-transfer transition and not a modified transition of one or other component. In practice the absorption characteristic of the complex in solution may not be easily observed since the complex will be partially dissociated into its component species. It may be particularly difficult to measure those absorption bands due to 'local excitation', when the interaction is between strong donor and strong acceptor. In such cases the transition usually appears as a separate band considerably at longer wavelength than the absorption of the component molecules. The intensity of absorption band of a complex is usually determined as the molar absorptivity (extinction coefficient) at the wavelength of maximum absorption. A direct determination of intensity can not normally be made because the degree of dissociation of the complex in solution is usually significant. Solid charge-transfer complexes have been studied by transmission³⁶⁻⁴⁶ and reflection⁴⁷⁻⁴⁹ spectra using specular reflection from a single crystal. Soon after the publication of Mulliken's charge transfer theory, Nakamoto⁵⁰ provided an experimental observation which could be well explained in terms of this theory, whereas the absorption of polarised light by oriented crystals and of pure aromatics shows a stronger low energy absorption when the electric vector is parallel than when it is perpendicular to the ring, the

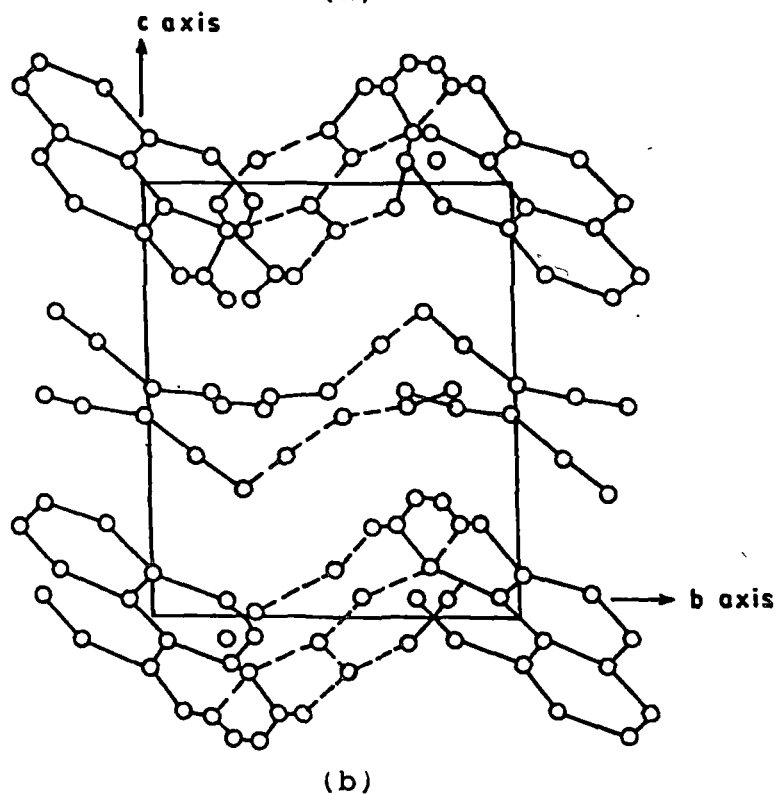
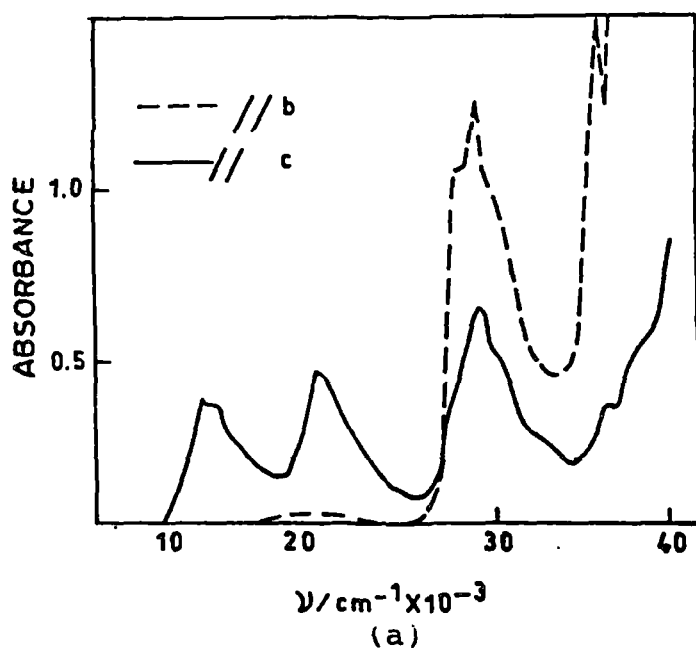


Fig. 1.4: The solid complex pyrene-tetracyanoethylene: (a) the polarized absorption spectra of a single crystal: (b) a projection of the crystal structure along the a-axis on the bc plane showing the orientation of the b- and c-axis.

opposite obtains for the lowest energy intermolecular charge-transfer transition of a complex between the two planer molecules (figure 1.4). If a number of donors are complexed with a single acceptor, a refined parabolic relationship of the form in equation (11) follows

$$h\nu_{CT} = I^D - C_1 + \frac{C_2}{I^D - C_1} \quad (11)$$

where C_1 and C_2 are constants for a given acceptor. This equation best correlated the data available then. As the range of donors is increased, some changes in these values can be expected. Slightly prior to the application of equation (11) McConnell et al.⁵¹ showed that there is an approximately linear relationship between I^D and ν_{CT} (frequency of CT band) for complexes of iodine with the wide range of relatively weak donors.

$$h\nu_{CT} = I^D - E^A - W \quad (12)$$

where E^A is electron affinity of the acceptor and W is the dissociation energy of the charge transfer excited state. Since the publication of that paper, similar linear relationships have been described for complexes of many other acceptors. In general

$$h\nu_{CT} = aI^D + b \quad (13)$$

when there is linear correlation between I^D and $h\nu_{CT}$, it is taken as

a confirmation of a charge-transfer complex, though there is no theoretical justification. There is a similar linear relationship between the electron affinity of series of acceptors, complexed with a single donor and $h\nu_{CT}$ of the type.

$$h\nu_{CT} = a E^A + b \quad (14)$$

The electron affinity of a number of acceptors has been evaluated from polarographic half wave potential by the equation

$$E^A = - E_{1/2}^{red} + 1.41 \quad (15)$$

The energy of charge-transfer band is correlated with the Huckel coefficients as follows:

$$h\nu_{CT} (A_1) - h\nu_{CT} (A_2) = B_j(A_1) - B_j(A_2) \quad (16)$$

where B_j is a Huckel coefficient.

Kosower⁵²⁻⁵⁵ has shown that, ν_{CT} for the complex between the iodide ion and a pyridinium ion is extremely solvent sensitive. For complexes in which the components are oppositely charged species, the ground state may be expressed as predominantly an ion pair with a small admixture of a structure involving of pyridinium radical and iodine atom with the two odd electrons coupled, i.e. $a^2 \ll b^2$ in equation:

$$\psi_N(AD) = a \underset{\text{no-bond}}{\psi_0(A,D)} + b \underset{\text{dative}}{\psi_0(A^{\cdot-}D^+)}$$

in contrast to the ground state of a weak complex formed of two neutral species where $a^2 \gg b^2$. The excited state of the pyridinium complex will be given by the equation

$$\psi_E = a^\# \psi_0(A,D) - b^\# \psi_0(A^--D^+)$$

where $a^{\#2} \gg b^{\#2}$.

I.R. Spectroscopy:

The CT studies in the solids and in solution state very clearly focus our attention on the differences in the two approaches. Thus infra-red measurements provide no information about relative orientation of the donor and acceptor in the complex solution. Infra red spectrum of the solid bromine benzene complex has enabled some modifications to be made to the crystal structure description determined by X-ray diffraction. The IR spectrum which includes a bromine-bromine stretching vibration is inconsistent with the crystal structure⁵⁶ having an axial configuration with chains of alternating benzene and halogen molecules, in which the halogens are equidistant from two neighbouring benzene molecules in the chain and are centres of symmetry. Person et al.,⁵⁷ suggested that these conflicting observations can be reconciled if, in the crystals the halogen molecules are not, infact, exactly equidistant from their immediate benzene neighbours in the chain, but are somewhat closer to one than the other.

The solid-state studies on the tetracyanoethylene (TCNE)

and hexamethylbenzene (HMB) system has been very rewarding. Two complexes with a mole ratio of 1:1 and 1:2 have been prepared.^{58,59} The infra red spectra of the two complexes are given in figure 1.5. The spectra of the 1:2 complex may be intercepted in terms of a structure which consists of stacks which contain sequences of D.A.D. . . . D.A.D. . . . D.A.D. . . . molecules. In the 1:1 complex the out of plane infra red spectrum shows no absorption at 1295 cm^{-1} (an absorption assigned to the totally asymmetric C-CH₃ stretching mode of HMB which is forbidden in the free molecule). This is to be expected in terms of Ferguson and Matsen's⁶⁰⁻⁶² and Person and Friedrich's⁶³ theory. Since the charge oscillator between D and A, characteristic of a vibronic interaction, is effectively zero in symmetrical D.A. . . . D.A. . . . D.A. . . . sequence of the 1:1 complex. However, in the 2:1 complex, the lower symmetry of the environment of the donor molecules permits the charge oscillation, and a strong absorption is observed at 1295 cm^{-1} . By contrast, the symmetry of environment of the TCNE molecule should be comparable to the 1:1 and 1:2 complexes. The similar absorption of the totally symmetric double bond mode of TCNE at 1560 cm^{-1} in the two complexes provides support for this conclusion.

The acceptors are generally classified as non-acidic and acidic compounds. The former type can only form DA complexes involving electron transfer while the acidic compounds are capable

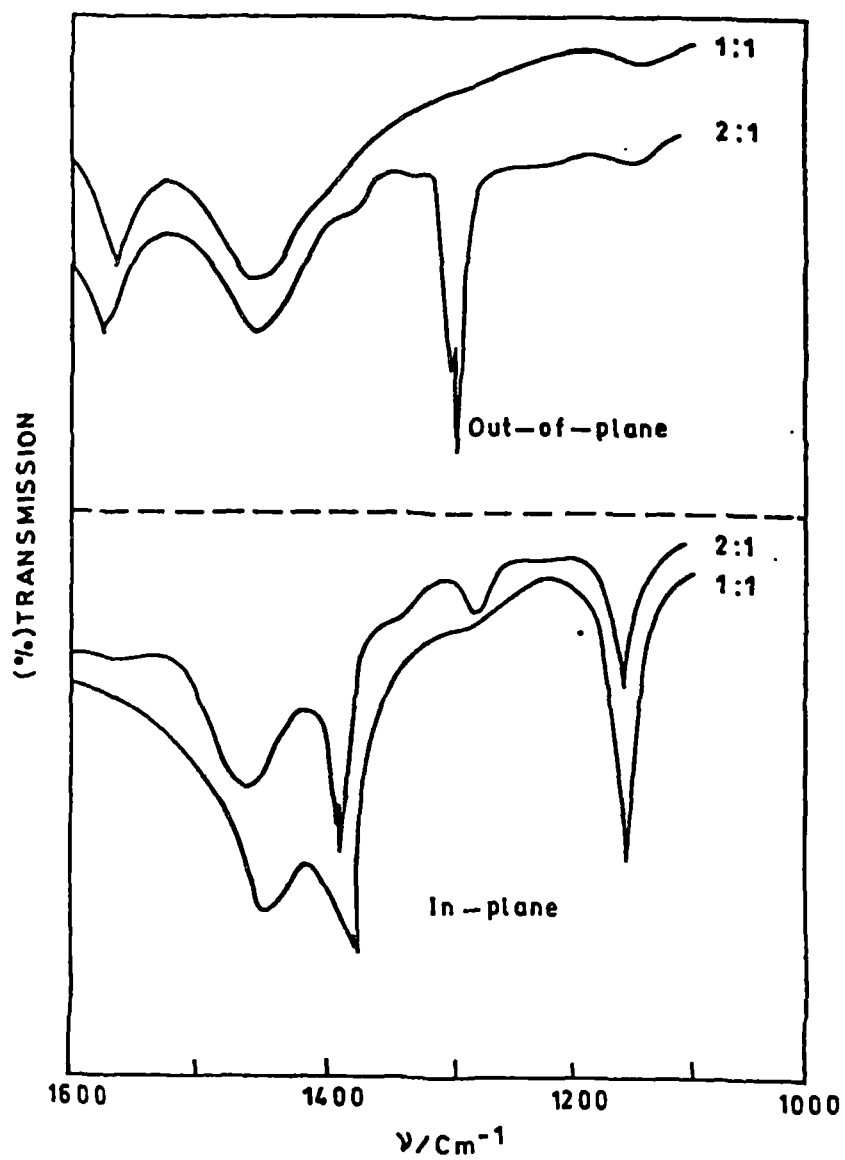
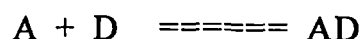


Fig. 1.5: Infrared spectra in the 1100-1600 cm^{-1} range for the 1:1 & 2:1 crystalline complexes of hexamethylbenzene and tetracyanoethylene.

of forming both the electron transfer complexes and those comprising proton donation to the donor. Most polynitroaromatics are non-acidic acceptors and, therefore, they are expected to display the general spectral shifts of $\pi - \pi^*$ complexes.⁶⁴ Since the stability of these complexes arises from a shift of the electron density from the donor to the electron deficient acceptor molecule, the infra-red region should record the effect of the change of electron density in the components upon the vibration of atoms within the individual molecules. Study of vibrational spectra may also reveal which parts of the molecules play an active role in complex formation.

Spectrophotometric Determination of Equilibrium constant and molar absorptivity:

The formation constant is defined for the reaction



by the expression

$$K = \frac{[AD]}{[A][D]} \dots\dots\dots (17)$$

Here, for example, $[D]$ is the concentration (in moles per litre) of the donor that exists in the solution at equilibrium. If we take solutions with fixed total concentration $[A]_0$ of A but with increasing concentrations of D, equation (17) implies that the concentration $[A]$ of the complex AD increases as shown in

figure 1.6. Since the absorbance A due to AD in a region in which the complex absorbs is given by Beer's Law.

$$A = \text{Log} \frac{I_0}{I} = \epsilon[AD]l$$

Here ϵ is the molar absorptivity of AD and l is the length in the centimeters of the absorbing path. The value of A must increase as $[D]$ increases, as is seen from figure 1.6, depending on how large K is, $[AD]$ at maximum possible donor concentration (region III of figure 1.6, $K > 1.0$) or be limited to region II ($K=0.1$) or even to region I ($K < 0.01$).

From the corrected absorbance A at a given frequency ν for a series of concentration $[D]$, the values of K and ϵ_ν can be obtained by using the method of Benesi and Hildebrand.⁸ The Benesi-Hildebrand analysis starts from the assumption that only one equilibrium exists in the solution and that the constant is defined as in (+) equation (1). Then, using a zero superscript to denote the total concentration $[D]_0 = [D] + [A]$, etc), we have

$$\frac{1}{K} = \frac{[D]_0 - [AD][A]_0 - [AD]}{[AD]} = \frac{[D]_0 [A]_0 - [D]_0}{[AD]} - [A]_0 + [AD] \quad \dots(18)$$

Under the usual conditions (K small, A relatively insoluble) $[D]_0$ is very much greater than $[A]_0$, in order to form enough complex:

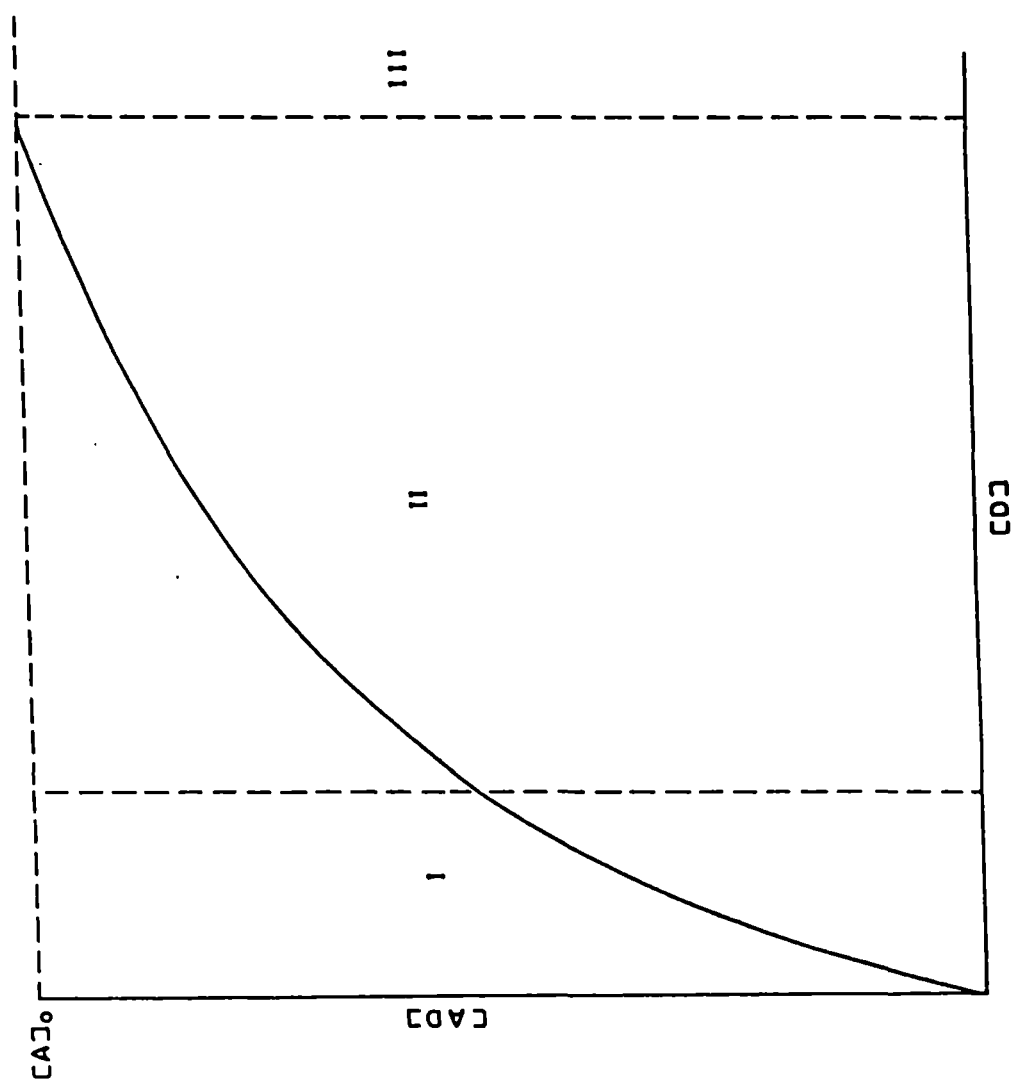


Fig.1.6: The concentration of complex as a function of donor concentration for a fixed total acceptor concentration $[A]_0$. Region I: $[AD]$ is approximately a linear function of $[D]$. Region II: Saturation has been reached, and $[AD]$ is constant and equal to $[a]_0$.

$[D]_0 \gg [A]_0 > [AD]$. From Beer's law $[AD] = A/\epsilon V$; hence to a good approximation.

$$\frac{1}{K} = \frac{1[D]_0 [A] \epsilon_v}{A} - [D]_0 \quad \dots (19)$$

Dividing by $[D]_0 \epsilon_v$ and representing, we obtain the Benesi-Hildebrand equation.

$$\frac{1[A]_0}{A} = \frac{1}{K\epsilon_v} \frac{1}{[D]_0} + \frac{1}{\epsilon_v} \quad (20)$$

Here, in a given experiment we know 1 , $[A]_0$ and $[D]_0$; A is measured for a series of solutions with varying $[D]_0$.

The above equation is not valid for sparingly soluble compounds because their conclusions can not be accurately determined, therefore, the Pushkin-Varshney-Kamoonpuri⁶⁵ equation was proposed to solve this problem. This equation takes the form.

$$\frac{1}{A} = \frac{1}{K\epsilon_v} \frac{1}{[A]_0} \frac{1}{[D]_0} + \frac{1}{[A]_0\epsilon_v} \quad (21)$$

If a plot is made of $1/A$ Vs $1/[D]_0$ a straight line is obtained and K is evaluated by dividing the intercept by the slope. Therefore, $[A]_0$ mutually cancels out and is not required for evaluation of K .

$[A]_0$ should be kept constant in all solutions.

Determination of Equilibrium Constant by I.R Spectrometry:

Though charge-transfer complexes have mainly been studied by uv-visible spectroscopy chiefly due to the possible isolation of the charge-transfer band, IR spectrometry can give an idea about the geometry of the complex. In most complexes and specially in the individual spectra. However, shifting of peaks may take place to lower or higher frequencies. The regions where there is a greater shift in electron density are the ones that give rise to more prominent peaks; enhanced intensity and greater magnitude in the frequency shifts.

IR spectrometry can also be used to determine the association constants using the usual Benesi-Hildebrand equation.

$$\frac{1[A]_0}{A} = \frac{1}{K\epsilon_v} + \frac{1}{[D]} + \frac{1}{\epsilon_v}$$

For this it is necessary that a peak is chosen which is not overlapped by other peaks and has maximum intensity. The transmittance is measured and converted to absorbance directly. IR spectrometry is a useful tool to distinguish between charge-transfer and hydrogen bonding. For example if aniline is involved in hydrogen bonding the N-H vibration in the complex will move to lower

frequencies while in the case of charge-transfer the reverse will be true. IR is also diagnostic of those CT complexes where there is almost complete transfer of the electron from the donor to the acceptor and highly conducting organic metals or semi conductors result. In this case there is usually no peak in the entire IR region.

Some Recent Developments in Charge-Transfer Complexes:

Equilibrium measurements have been used for the evaluation of ionization potentials.⁶⁶ Though such studies leave much to be desired by way of accuracy, nevertheless they are important due to their inherent simplicity. Through space interactions and reactivity have been related by studying the photoelectron and charge-transfer spectra of benzobicycloalkenes.⁶⁷ Studies in micellar media are gaining a unique importance in chemistry and therefore it is interesting to note, a recent report showing the effect of micelles on the state and dynamics of some excited charge-transfer complexes.⁶⁸ The formation constants of selected CT band complexes have been measured using a computer controlled precision polarograph.⁶⁹ It has been seen that Flavin mononucleotide forms charge-transfer complexes with phenols. This has been established through the use of resonance Raman spectroscopy.⁷⁰ A single crystal of the charge-transfer complex between hexaethylbenzene and tetracyanoethylene was investigated for conformational effects and charge-transfer transitions.⁷¹ Conducting organic charge-transfer

complexes are of current importance due to their possible use as organic conductors, semiconductors and, therefore, it is interesting to note that the charge-transfer salts synthesized by the reaction of tetrathiafulvalenes and tetrahalo-p-benzoquinones produced highly conducting organic materials.⁷² It was shown that the complexes of phenyl-furans and tetracyanoethylene were π - π^* complexes.⁷³ In an excellent study it has been shown that some charge-transfer complexes of tetracyanoquinodimethane can be used to prepare electrochemical electrodes which can be used over a potential region where they serve as inert electrodes.⁷⁴ Most of the organic conductors to date have been based on tetracyanoquinodimethane. Therefore, it is very encouraging to note that the charge-transfer compounds composed of tetrathiafulvalene and chloranil are perhaps the first highly conducting organic materials that do not contain tetracyanoquinodimethane.⁷⁵ IR spectroscopy has been used to study the degree of charge-transfer in organic conductors.⁷⁶ n - π^* charge-transfer complexes are now systematically being studied due to the paucity of such studies on this important family of complexes. For example, the interaction of aliphatic amines and benzonitrile has been reported.⁷⁷ The solvent effects on the charge-transfer spectra of some amino anthraquinone dyes has been reported in nine different solvents.⁷⁸ Surface enhanced Raman scattering shows that there is a charge-transfer from tetrathiafulvalene to silver and gold.⁷⁹ The

formation of a charge-transfer complex between quinoline and boron tetrafluoride lead to significant changes in the ordering of electronic levels affecting fluorescence, phosphorescence and inter-system crossing.⁸⁰ The mechanism of electron transfer from dihydronicotinamide adenine dinucleotide (NADH) to p-benzoquinone derivatives has been shown to proceed via a charge-transfer complex.⁸¹ Picosecond Laser photolysis has been used to establish the charge-transfer process that occurs in the dibenzocarbazolepyridine hydrogen bonded complexes as a function of structure.⁸² The 1:1 and 2:1 complexes of hexamethylbenzene with tetracyanoethylene have been studied by resonance Raman spectroscopy.⁸³ The colour of (nitrophenyl) anilines has been explained from an X-ray crystallographic study that indicates that the molecules are placed in a 'head to tail' arrangement resulting in an unusual charge-transfer between two molecules of the same compound.⁸⁴ Some large electron acceptors based on various substituted quinodimethanes have been designated as acceptors for molecular metals.⁸⁵ The study of vapour phase charge-transfer complexes is rather difficult owing to the sophistication and cost of instrumentation. It is due to this reason that not much progress has been made in this important direction. It is therefore encouraging to note that electron energy loss spectroscopy has been used for the investigation of vapour phase charge-transfer complexes of halogens with n-donors.⁸⁶ Graphite coated with viologen polymers behaves as

an electrode via a charge-transfer process.⁸⁷ Charge-transfer complexes have been used for the synthesis of organic ferromagnetic materials.⁸⁸ The tetramethylamine-sulphurdioxide system is the only system for reaction thermodynamics known both in solution and gas phase. The microwave spectrum of this system has been studied in order to elucidate the structure of the complex.⁸⁹ The reaction of azoalkanes with series of donors which are both sacrificial (π^* , σ^*) and increvalent gives rise to charge-transfer complexitation.⁹⁰ The fluorescence spectrum of benzenilide exhibits the anomaly that its λ_{max} occurs at longer wave lengths than that of its phosphorescence emission. It has recently⁹¹ been shown that this anomaly may be due to an inter-molecular charge-transfer transition. A new approximate procedure for the determination of enthalpy of formation and formation constants of weakly bonded charge-transfer complexes has been reported and has been applied to complexes of molecular iodine and chlorinated benzenes.⁹² The effect of solvent on dipole moment and charge-transfer in electron system has been studied in N, N-dimethyl-p-nitrosoaniline.⁹³ ¹H NMR spectrometry⁹⁴ has been used to evaluate association constants for the electron-donor-acceptor complexes for the complexes of indoles and substituted indoles with 1-(2,4,6-trinitrophenyl) propan-2-one. It has been suggested that both internal and external references may be eliminated in NMR

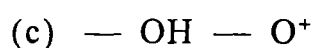
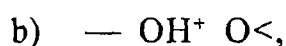
determinations of fast equilibria with special reference to charge-transfer complexes.⁸⁵ This study also questions the use of tetramethylsilane(TMS) as an internal reference due to the possibility that TMS may not be as inert as assumed. A new and simple development for the measurement of charge- transfer through fibre optic photometry has been proposed.⁹⁶ The preparation and solid-state characterization and X-ray crystal structure of the 1:1 charge-transfer complex of tetrathiafulvalene and m-dinitrobenzene is an important landmark in the study of charge-transfer complexes of polynitroaromatics.⁹⁷

Hydrogen-Bonding:

Many investigations have been carried out on the inter and intra-molecular interactions among proton donors like -OH, -NH₂, etc., and proton acceptors such as amines and oxo-compounds. It has been well verified that hydrogen bonding in molecular complexes (e.g., as—OH . . . O<) is formed between proton donors and acceptors. Since atom participating in the hydrogen bond formation are usually electronegative atoms such as F (halogen, O, and N, and moreover since a hydrogen atom has a small size, which makes it possible for it to occupy a position closer to a proton acceptor than can other elements, the force to bring about the hydrogen bonding has been mainly attributed to the electrostatic force. For instance,

energy calculations according to the electrostatic model were made by Coggeshall⁹⁸ for some hydrogen bonding system. The results of the calculations seemed to be in satisfactory agreement with experimental ones. However, it is supposed that there is no reason to reject the contribution from the covalent bonding interaction nature to the hydrogen bond formation. The covalent bonding nature has been a central problem of the experimental and theoretical studies of hydrogen bonding since about 1950. Among many workers this problem was especially discussed by Mulliken,⁹⁹⁻¹⁰¹ Nagakura et al.,^{102,103} Coulson and Danielsson,¹⁰⁴⁻¹⁰⁶ Tsubomura,¹⁰⁷ Pimental¹⁰⁸ and Murrell et al.¹⁰⁹

In valence bond language the main resonance forms of a hydrogen bonding system would be written as below, for a typical example of an $O - H \cdots O$ systems.



Here, structures (a) and (b) correspond to the no-bond structure in terms of charge-transfer theory. Structure (a) means a pure covalent pairing between an oxygen orbital and a hydrogen

orbital. Structure (c) is a purely ionic structure of the OH bond and could mainly cause an electrostatic interaction with a proton acceptor. Structure (c) is a charge -transfer structure where the long covalent bond is formed between the H atom and the oxygen atom of proton acceptor. This structure (c) should play an important role in the covalent nature of hydrogen bonding.

Of course there are other resonance forms such as:

(d) — $\text{O}^+\text{H}^-\text{O}$ and

(e) — OH^-O^+

The contributions from these resonance structures, however, seem to be smaller than those from the structures (a), (b) and (c), hence chemical and physicochemicals evidence shows the O—H bond to have polarisation $\text{O}^{\delta-}\text{—H}^{\delta+}$.

In molecular orbital language the contribution from the charge-transfer resonance structure (c) would be explained as follows: when one takes into account only the O—H σ bond and the lone pair orbital of proton acceptors, the mutual relation of energy levels among the σ bonding, σ antibonding, and the lone pair orbital may be illustrated as in figure 1.7.

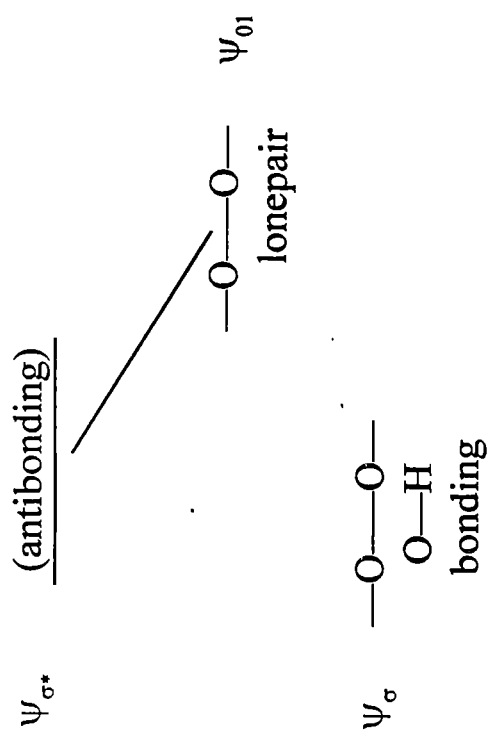


Fig. 1.7 : Simple MO description of hydrogen bonding system, $\text{O}-\text{H}\cdots\text{O}<$.

Resonance structure (c) should be due to an electron transfer from the ψ_{01} orbital to the σ^* antibonding orbital. Because of the antibonding nature of the σ^* orbital the aforementioned electron transfer should inevitably weaken the OH bond, as can be seen in the resonance structure (c), so that the O—H σ bond distance becomes longer than in the normal one, and a new and long H—O δ^+ bond is formed.

These results will cause a double minimum potential to the hydrogen bonding system. It should be now noted that the characteristic of the antibonding σ^* orbital of an O—H group and that of halogen molecules like iodine are somewhat similar to each other, as indicated in figure 1.8. Thus the n— σ type halogen complex or the n— σ type hydrogen bonding complex will be formed so as to satisfy the maximum overlap between the plus lobe (K) or l shown in figure 1.8 and the no bonding electron donor orbital. Therefore, we can understand that the geometrical arrangements of the n— σ type halogen complex and hydrogen bonding complex are quite similar to each other.

The theoretical considerations show that the contributions of the charge-transfer type of force can not be neglected as a source of hydrogen bonding energy. Many expected facts supporting this view

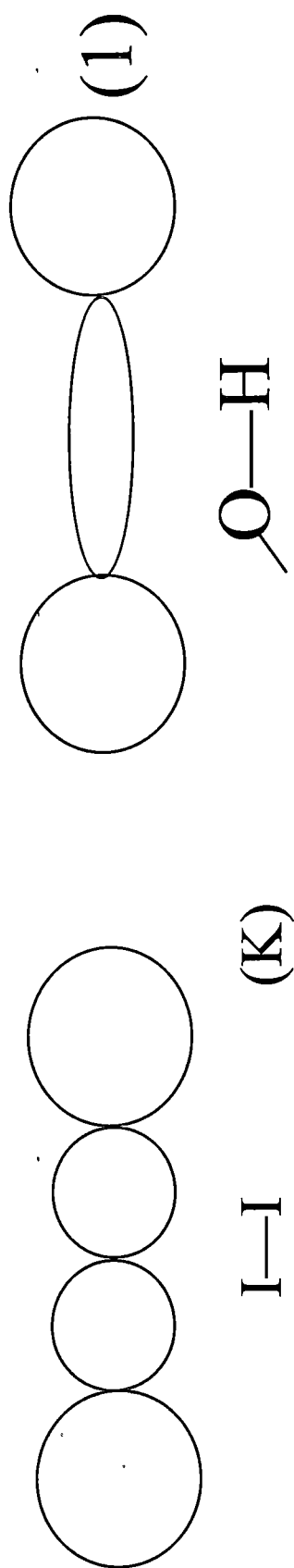
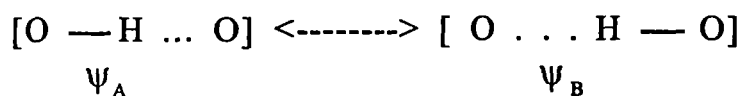


Fig. 1.8 Schematic representation of σ^* antibonding orbital of I_2 and O—H bond. Each size means the negative part of orbitals.

point have been reported by many workers. From the concept of charge-transfer theory the charge-transfer energy pertinent to hydrogen bonding may be mainly attributed to consideration of the quantum mechanical resonance between the following two resonance forms: $[X-H \dots Y] \longleftrightarrow [X^- \dots H-Y^+]$. The nature of the electronic interaction in the hydrogen bonding and the $n-\sigma$ type charge-transfer complexes is quite similar. Therefore, it seems to be quite reasonable to expect the appearance of the charge-transfer spectrum due to the hydrogen bonded complex in a suitable wavelength region, depending on the nature of the hydrogen bonding system. The effort to detect the charge-transfer spectra pertinent to hydrogen bonding was carried on by many workers. But clear detection of this kind of charge-transfer spectra was found to be quite difficult because, the charge-transfer spectra possibly occur in a region of the far-UV (less than 220 m μ). Where electronic spectra originating, e.g., from a $n-\sigma^*$ type transition or a Rydberg transition appear. Moreover, quantitative measurement of absorption spectra is not so easy in the far - UV region.

Among the structure of hydrogen bonding reported up to now, however, there is an example of the charge-transfer spectrum caused by relatively strong intra-molecular hydrogen bond of mononegative ion of maleic acid (MNMA).¹⁰³

Because of the symmetrical structure of the hydrogen maleate anion the hydrogen atom participating in the hydrogen bonding is placed at the mid-point between two oxygens. Actually this structure has been confirmed by X-ray analysis of crystalline MNMA.^{110,111} Atomic orbitals participating in the system of the hydrogen bond O --- H --- O are in the molecular plane of MNMA and are perpendicular to the π type atomic orbitals (π electron system). Therefore, the electronic interaction in the hydrogen bond will be approximately represented by the resonance between two structures with equal energies.



Mutual interaction between ψ_A and ψ_B produced two new wave functions, ψ_N and ψ_E , the former being for ground state with eigen-value W_N and the latter for the excited state having the energy W_E .¹⁰³

$$\psi_N = \frac{1}{\sqrt{2(1+S_{AB})}} (\psi_A + \psi_B) \quad (22)$$

$$\psi_E = \frac{1}{\sqrt{2(1-S_{AB})}} (\psi_A - \psi_B) \quad (23)$$

W_N and W_E are now given by usual method:

$$W_N = \frac{H_{AB}}{1+S_{AB}} \quad \text{and} \quad W_E = \frac{-H_{AB}}{1-S_{AB}} \quad (24)$$

Here, the energy of ψ_A and ψ_B is taken as a standard (energy zero). Thus the energy of the charge-transfer spectrum becomes

$$W = W_E - W_N = \frac{-2H_{AB}}{1-S_{AB}^2} \quad (25)$$

and the oscillating strength is calculated using the well-known equation

$$f = 1.085 \times 10^{-5} \times V_Q^2 \quad (26)$$

where V is the transition energy (cm^{-1} Unit) and Q is the transition dipole length (\AA unit). Remembering the ψ_A or ψ_B in equation (22) and (23) the calculation¹⁰⁴ of S_{AB} results in $2(S_{OH})_2$, where S_{OH} means the overlap integral between approximate atomic wave functions for the oxygen and hydrogen atoms. Thus Nagakura¹⁰³ evaluated the Oscillator strength f , using the calculated value (0.279) of S_{OH} and the observed charge-transfer maximum 211 $\text{m}\mu$, $f=0.78$ being obtained. This result may suggest that the charge-transfer spectrum brought about by hydrogen bonding should have quite strong intensity. Experimentally, the UV spectra of the hydrogen maleate

anion were examined by Nagakura at various P^H values in aqueous solution and also by the measurement of polarized spectra of the single crystal of potassium hydrogen maleate, the data being depicted in figure 1.9 and 1.10.¹⁰³

Curve 1 in figure 1.9 is for maleic acid (MH_2), curve 2 for the monoanion (MH^-), and curve 3 could be due to the dianion (M^{2-}) plus a small quantity of MH^- . It is now certain from figure 1.7 and 1.8 that the absorption band due to MH^- is in high intensity and that the 211 $m\mu$ band of MH^- shows stronger absorption with the light polarized along the c-axis than when along the b-axis. The combination of these spectral data with those X-ray analysis of the MH^- crystal led to the conclusion that the 211 $m\mu$ band is polarized along the O—H ... O bonds.

Moreover, it should be noted that the $\pi-\pi^*$ absorption band of the species M^{2-} should appear at a wavelength longer than that of the species MH^- , the result of the theoretical P.P.P. type calculation supported this conclusion.¹⁰³ Since it is clear from figure 1.8 that the 211 $m\mu$ band in question shifts to a shorter wavelength in the medium where the molecule exists predominantly as the M^{2-} species, the assignment of the 211 $m\mu$ band to the $\pi-\pi^*$ transition may not be reasonable.

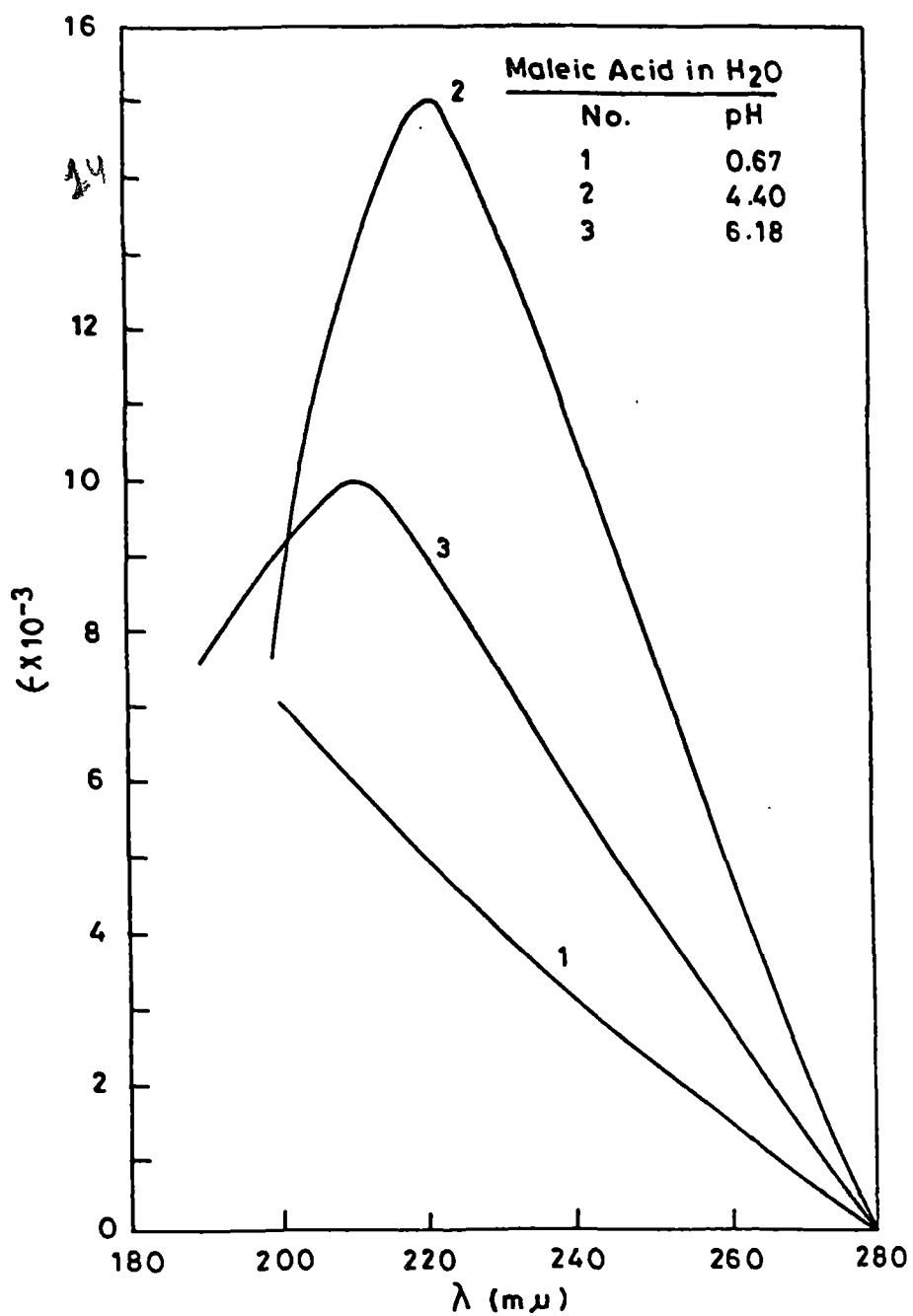


Fig. 1.9: Absorption spectra of aqueous solutions of maleic acid at pH = 0.67 (Curve 1), pH = 4.40 (Curve 2), and pH = 6.18 (Curve 3).

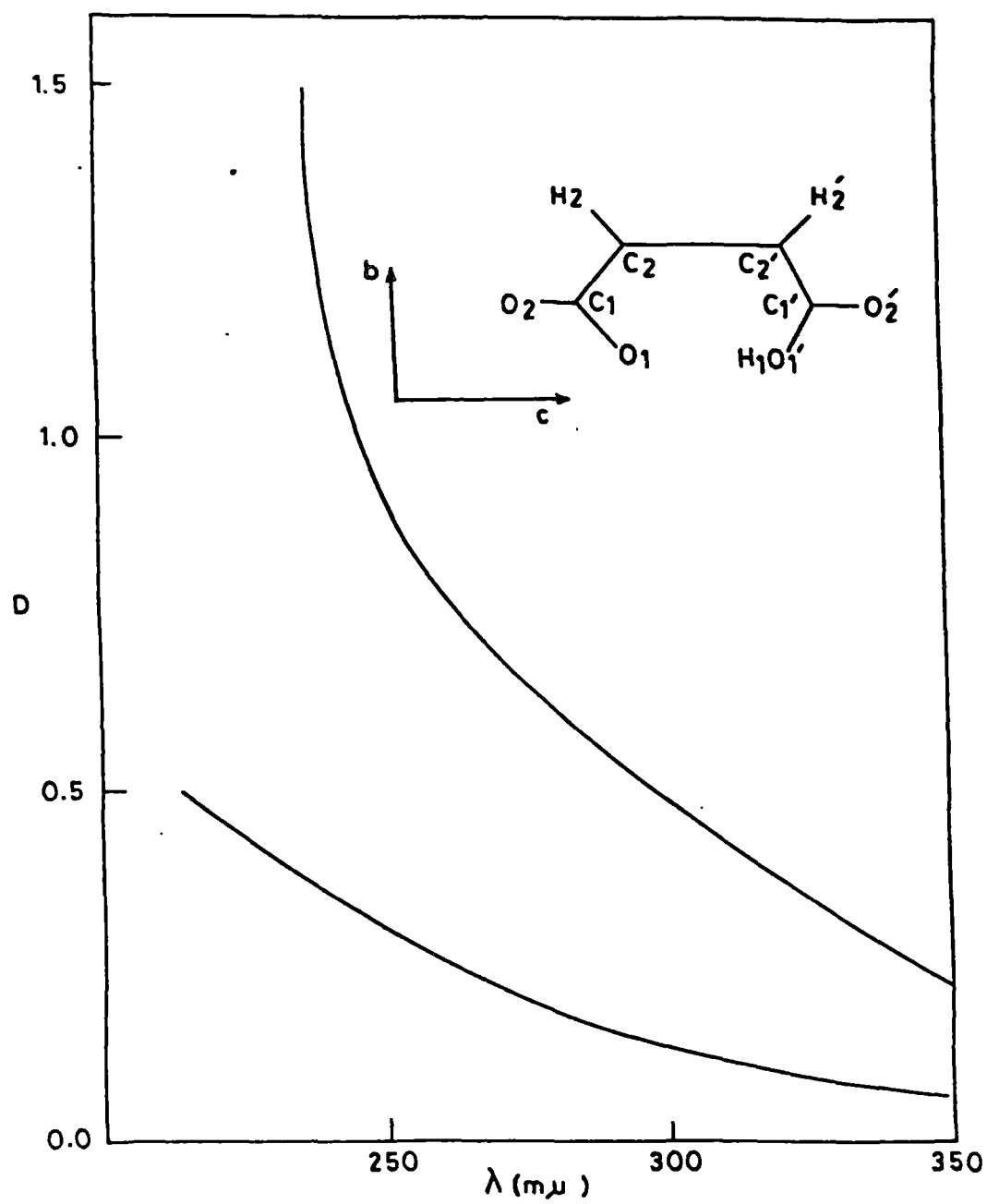


Fig.1.10: Polarized ultraviolet absorption increases with a potassium hydrogen maleate single crystal.

Charge-transfer forces play an important role in the hydrogen bonding interactions. Some experimental results which support this conclusion will be described in this section. One examines the proton accepting power of some typical compounds. First, are triethylamine, diethylether, and nitromethane.¹¹² The dipole moment of these compounds increases in this order, as is seen in Table 3 where many data are collected for comparison. If the nature of the hydrogen bond is essentially electrostatic, then one supposes that the hydrogen bonding power is of the order of $\text{CH}_3\text{NO}_2 > \text{O}(\text{C}_2\text{H}_5)_2 > \text{N}(\text{C}_2\text{H}_5)_3$. Actually, however, this is not the case, as Table-3 shows. So the electrostatic interaction seems not to be the main source for the present hydrogen bonding interaction. On the other hand, the ionization potential I_p in the order:

$\text{N}(\text{C}_2\text{H}_5)_3 < \text{O}(\text{C}_2\text{H}_5)_2 < \text{CH}_3\text{NO}_2$. This order is just reverse of the observed one of the hydrogen bonding ability i.e. $\text{N}(\text{C}_2\text{H}_5)_3 > \text{O}(\text{C}_2\text{H}_5)_2 > \text{CH}_3\text{NO}_2$ but is in agreement with that predicted by equation (27).

$$\Delta E = - \frac{2\beta_y^2 - H_x}{I_y - A_{x-H}} \quad (27)$$

Where ΔE is delocalization energy, I_y and A_{x-H} are the ionization potential of the occupied orbital of the proton acceptor

Table-3
HYDROGEN BONDING AND IODINE COMPLEXING ABILITIES AND OTHER NATURES OF SOME ELECTRON
DONORS

Proton Donor	Proton Acceptor	Equilibrium Constant K(litre/mole)	Shift of absorption Spectra of proton	Acceptor I _p (ev)	PK _a	Dipole moment
β-naphthol	N(C ₂ H ₅) ₃	103 (25° C)	590 (¹ L _b band)	7.5	10.72	0.82
n-heptane	O(C ₂ H ₅) ₂	14.5 (25° C)	410 (¹ L _b band)	9.53	-3 to -3.61	1.13
	CH ₃ .NO ₂	2.6 (25° C)	190 (¹ L _b band)	10.33	-11.38	3.50
				11.32		
β-naphthol	N(C ₂ H ₅) ₃	180 (~15° C)	590 (¹ L _b band)	7.5	10.72	0.82
(Cyclohexane)	CH ₃ COOC ₂ H ₅	14 (~15° C)	310 (¹ L _b band)	10.09	-6.2	1.83
	CH ₃ CN	9 (~15° C)	200(¹ L _b band)	12.39		3.92
						3.47

Electron/Donor	Electron Acceptor	Equilibrium Constant K/mole/litre	Heat of Formation (K Cal/mole)	PK _a of electron donor
N(C ₂ H ₅) ₃	I ₂ (n-heptane)	6460 (20° C)	12	10.72
	I ₂ (n-heptane)	41.0 (11° C)	8.2	5.21
C ₆ H ₅ .C≡N	I ₂ (CCl ₄)	0.81 (20° C)	--	--

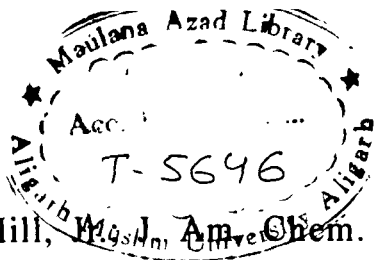
and electron affinity of the vacant σ^* orbital of the X-H bond respectively, β_y-H_x is the resonance integral between the ψ_o and ψ_{σ^*} orbitals, which describes the stabilization energy of the hydrogen bond due to the charge-transfer mechanism. Therefore, it seems that the charge-transfer force will contribute more predominantly to the hydrogen bonding systems mentioned above. The same conclusion as has been described above was also derived from the comparison of the proton accepting power among triethylamine, ethyle acetate, and acetonitrile.¹¹³ The values of the equilibrium constant K of the hydrogen bond formation with β -naphthol in the ground state are in the Table-3 of $(C_2H_5)_3 N > CH_3 COOC_2H_5 > CH_3CN$. Since the order of I_p is $(C_2H_5)_3 N < CH_3OOC_2H_5 < CH_3CN$, again decreasing the value of the equilibrium constant K. Furthermore, the red shift of the 1L_b band of β -naphthol caused by the hydrogen bonding interaction is largest in the case of $(C_2H_5)_3N$ and smallest for CH_3CN .

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CHAPTER - 11

**DETECTION OF SOME NITROGEN COMPOUNDS
AND THE SEMIQUANTITATIVE DETERMINATION
OF DIPHENYLAMINE WITH
p-DIMETHYLAMINOBENZALDEHYDE
BY CAPILLARY SOLID-STATE SPOT-TESTS**

Introduction:

It has been shown that the reaction between p-Dimethylaminobenzaldehyde (p-DAB) and diphenylamine can be studied in the solid-state by a simple technique.¹ In this chapter data are presented which throw light on the mechanism of the reaction between p-Dimethylaminobenzaldehyde² (p-DAB) and Diphenylamine. For this purpose measurements have been made at various temperatures and for particle of different sizes. The studies have been extended to other hydrocarbons such as phenanthrene and anthracene. As reported earlier the reactions are diffusion-controlled. Diffusion may occur by various mechanism such as lattice diffusion, vapour phase diffusion, surface migration, or grain boundary diffusion.

Interest in solid-state chemistry is growing.³⁻⁷ Solid-state reactions have much to offer to chemists concerned with synthesis, reaction mechanism or the chemistry of natural process. Feigl^{8,9} has shown some possibilities of using solid-state reactions in qualitative organic analysis. There include hydrolytic and ammonolytic cleavages, and displacement, condensation and redox reactions that occur when organic compounds are melted or sintered with suitable reagents. p-Dimethylaminobenzaldehyde (p-DAB) is a useful reagent in organic analysis. It gives coloured products and also produces fluorescent¹⁰ compounds in solution. We earlier proposed p-DAB in

the presence of hydrochloric acid for the specific detection of diphenylamine.¹¹ The mechanism and kinetics of this reaction in the solid state were investigated later.¹² It was found to be a diffusion-controlled reaction, a coloured boundary is formed at the junction of the two reactants and the diffusing species is $\text{Ph}_2\text{NH}_2^+\text{Cl}^-$.

It was therefore considered worthwhile to use the formation of a coloured boundary for the detection of organic compounds in the solid-state. For this purpose a new technique for solid-state spot-tests, called capillary spot-tests, was devised. This technique is very simple and can be used for semiquantitative determinations as well. This report summarizes the results obtained. Diphenylamine was also semiquantitatively determined by this technique.

EXPERIMENTAL:

Procedures:

Solid State Detection: A well powdered and thoroughly mixed mixture of p-Dimethylaminobenzaldehyde (P-DAB) and Potassium Hydrogen Sulphate (PHS) in equimolar ratio was used as the reagent (A). A little of the solid was mixed in a micro test-tube with several mg of A. The colour developed at room temperature (25°) as well as on heating was recorded. For heating the tube was placed for a few second in a water-bath preheated to 100°. The limits of identification were determined by starting with known volumes of

standard solutions of the compound concerned, evaporating to dryness at 100°, and mixing the solid residue with A.

A capillary (1 mm bore) was part-filled with A by continuous tapping and then the solid test material was added at the open end. The colour and fluorescence of the product at the junction were recorded. The limits of identification were determined by starting with various synthetic mixtures of the solid test materials with starch.

Capillaries containing A and solid test material (various concentrations of diphenylamine) were kept at 40° in an oven for 5 hr, and the length of the coloured boundary formed at the junction was recorded. A plot of diphenylamine concentration Vs. boundary length (figure 2.1 and figure 2.2) was linear but did not pass through the origin. The sensitivity is rather poor, 10% of diphenylamine giving a length of 1.0 mm and 100% giving 3.5 mm.

Capillaries containing A and solid test material (0.1-10% diphenylamine) were kept at room temperature for 2 hr or at 40° in an oven for 15 minute and the colour intensities were compared visually, both are cedures are quality good but it is faster, of course to use heating. The colour intensity is proportional to the concentration of diphenylamine.

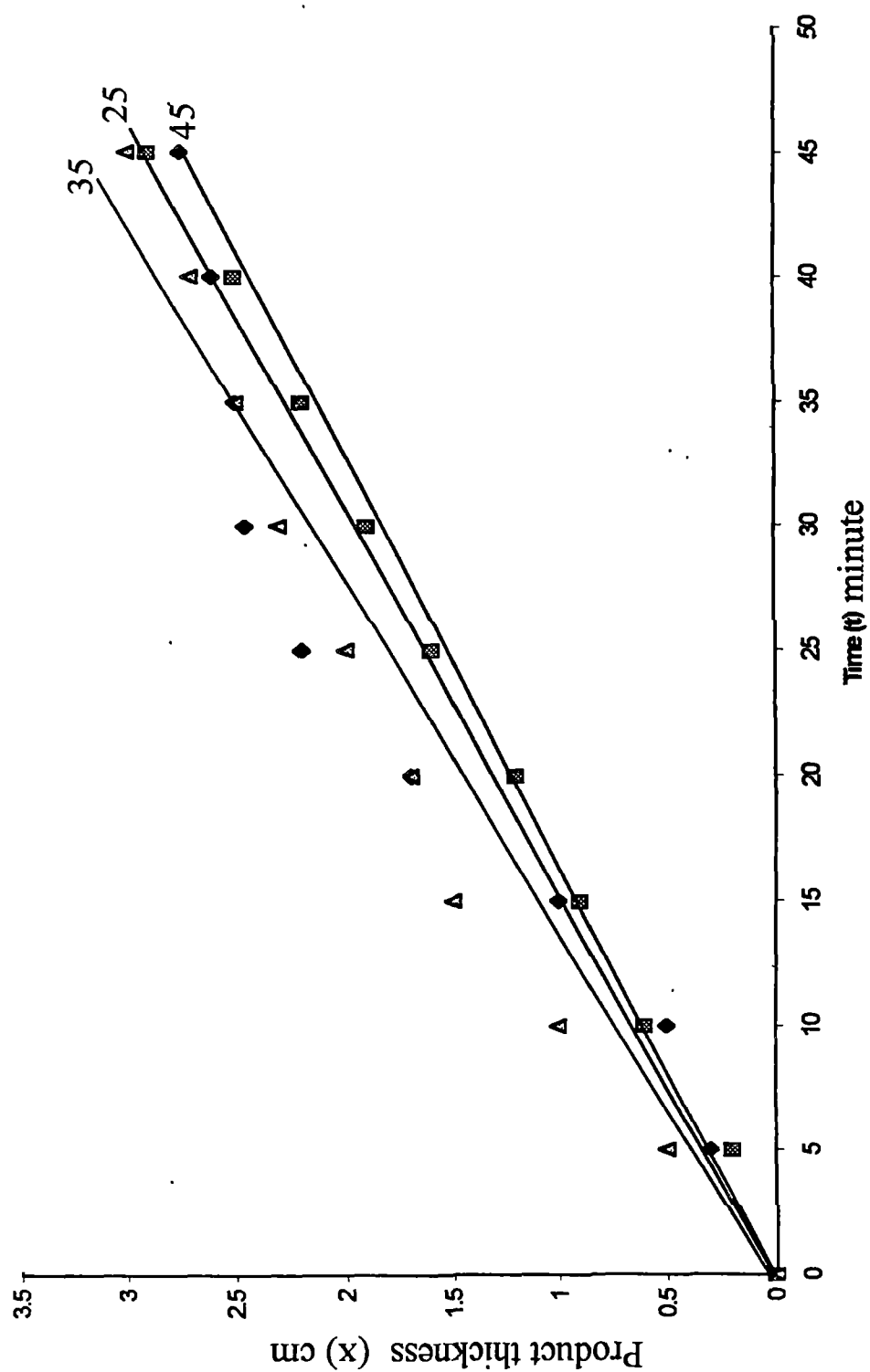


Fig. 2.1 Plot of product thickness verses time for the solid state reaction between p-DAB-Diphenylamine at the temperature 25, 35 & 45°C.

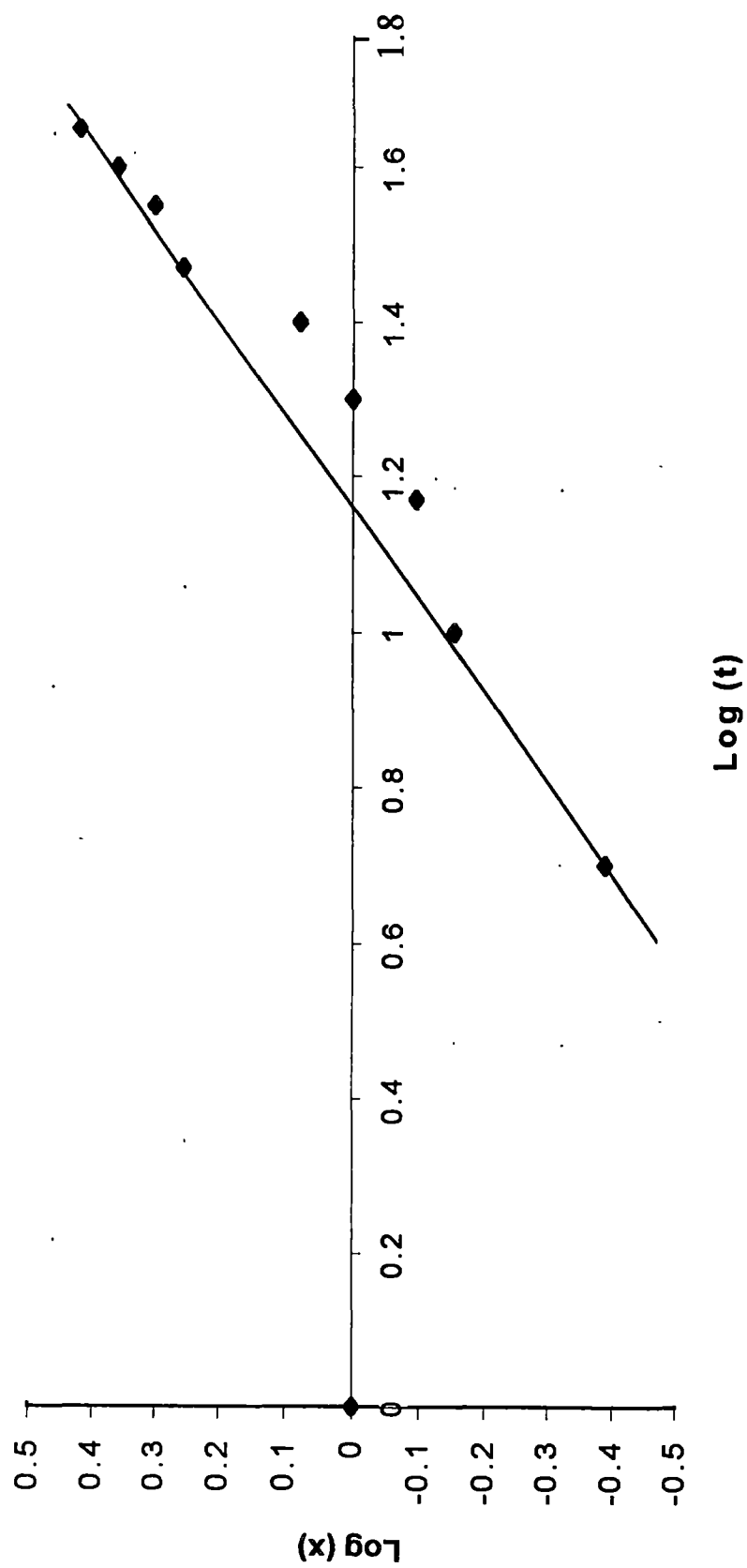


Fig. 2.2 Log of product thickness verses Log of time for the solid state reaction between p-DAB-Diphenylamine at the temperature 25°C.

Table - 1 (a)
(p-DAB+ PHS) A+Diphenylamine

Temp. at 20°

Sl.No.	Time (t) (min)	Log (t)	Scale	Actual Distance (x)	Log (x)
1	0	0	8.1	0	0
2.	5	0.78	8.5	0.4	—0.39
3.	10	1.0	8.8	0.7	—0.15
4.	15	1.18	8.9	0.8	—0.09
5.	20	1.30	9.1	1.0	0
6.	25	1.40	9.3	1.2	0.08
7.	30	1.48	9.9	1.8	0.26
8.	35	1.55	10.1	2.0	0.30
9.	40	1.60	10.4	2.3	0.36
10.	45	1.65	10.6	2.5	0.41

Table - 1 (b)
(p-DAB+ PHS) A+Diphenylamine

Temp. at 30°

Sl.No.	Time (t) (min)	Log (t)	Scale	Actual Distance (x)	Log (x)
1	0	0	6.8	0	0
2.	5	0.69	7.0	0.2	—0.69
3.	10	1.0	7.4	0.6	—0.22
4.	15	1.18	7.7	0.9	—0.46
5.	20	1.30	8.0	1.2	0.79
6.	25	1.40	8.4	1.6	0.20
7.	30	1.48	8.7	1.9	0.28
8.	35	1.55	9.0	2.2	0.34
9.	40	1.60	9.3	2.7	0.40
10.	45	1.65	9.7	2.9	0.46

Table - 1 (c)
(p-DAB+ PHS) A+Diphenylamine

Temp. at 45°

Sl.No.	Time (t) (min)	Log (t)	Scale	Actual Distance (x)	Log (x)
1	0	0	8.3	0	0
2.	5	0.78	8.5	0.3	—0.52
3.	10	1.0	8.8	0.5	—0.30
4.	15	1.18	9.3	1.0	0
5.	20	1.30	10.0	1.7	0.23
6.	25	1.40	10.5	2.2	0.34
7.	30	1.48	10.75	2.45	0.39
8.	35	1.55	10.8	2.5	0.40
9.	40	1.60	10.9	2.6	0.41
10.	45	1.65	11.0	2.75	0.43

Table - 2 (a)
Detection of Various Nitrogen Compounds with Reagent A

Compound	Solid State Reaction Colour		Solution Reaction Colour	
	Hot	Cold	Hot	Cold
Diphenylamine	Y	G	-	Y
α -Naphthylamine	Y	G	-	-
β -Naphthylamine	Y	G	Y	Y
O-Toluidine	O	O	Y	Y
p-Toluidine	Y	G	Y	Y
O-Nitrobenzoic Acid	Y	Y	Y	Y
m-Nitrobenzoic Acid	Y	Y	Y	Y
p-Nitrobenzoic Acid	Y	Y	Y	Y
O-Nitrophenole	Y	YG	-	-
p-Nitrophenole	Y	Y	-	-
O-Nitroaniline	Y	Y	Y	Y
m-Nitroaniline	Y	Y	Y	Y
p-Nitroaniline	Y	Y	Y	Y
Urea	RY	RY	Y	Y
Phenyl Urea	Y	YG	Y	Y
Benzamide	Y	Y	-	-
8-Hydroxyquinoline	Y	YG	Y	Y

Note: Y=Yellow, G=Green, O=Orange, R=Red

Table - 2 (b)
Contact Reaction Results in Capillaries with Reagent A at 50°C

Compound	Colour for	
	2% Concentration	10% Concentration
Diphenylamine	Y-O	O-O
p-Toluidine	Y-O	Y-O
O-Toluidine	Y-O	O-O
α -Naphthylamine	Y-DY	O-O
β -Naphthylamine	O-G	G-G
O-Nitrobenzoic Acid	-	LG-LG
p-Nitrobenzoic Acid	-	Y-Y
O-Nitrophenole	-	Y-B
p-Nitrophenole	-	O-R

Note: Y=Yellow, G=Green, O=Orange, R=Red, L=Ligh, D=Dark, B=Brown

The first letter refers to the initial colour and the second to that after 48 hrs.

Result and Discussion:

The result in table-1 indicate that the solid-state reactions are sufficiently sensitive, and can be used to distinguish similar compounds by means of the colours obtained in the cold and on heating.

It is known¹³ that many reactions which take place in solution are also observed in the reactions between the solids, particularly on trituration, where there is a close contact between the reacting substances. It is also known that many reactions between solids take place on simple contact of the reacting substances. This means that many compounds can be distinguished by solid-state contact reactions in a capillary, cf. table-2.

Further, of the substances tested only acridine, p-toluidine and semicarbazide hydrochloride form products with reagent A which give fluorescence in the capillary, the colours being OY, Y and Y respectively and the limits of identification 5,20 and 100 μg .

However, the method is not specific for detection of nitrogen compounds. For example, aliphatic amides do not react, nor do uracil, uric acid, adenine, glycine, phthalimide, sarcosine, EDTA, thebaine, papaverine, purines, α -amino-acids and pyridine derivatives. On the other hand, some compounds react although they do not contain nitrogen, e.g., Fleig¹⁴ and Van Urk¹⁵ found various such colour reactions of p-DAB, and we found that santonin, resorcinol, phloroglucinol and hydroquinone react.

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CHAPTER - 111

**DETERMINATION OF O-NITROANILINE WITH
p-DIMETHYLAMINO BENZALDEHYDE (p-DAB) BY
CAPILLARY SOLID-STATE SPOT TEST AND
DETERMINATION OF CHARGE-TRANSFER (CT)
COMPLEXES**

INTRODUCTION:

Reactions in the solid-state are a class by themselves. Because of difficulties in analysis of the composition of the solid phase, studies have been confined mainly to those cases where the course of reaction could be followed by x-ray crystallographic methods or by measuring the amount of gas evolved in suitable reactions.¹ The present note describes a new technique for studying the kinetics of reaction between p-DAB and O-Nitroaniline in the solid state by following movement of the coloured interface which apparently gives worthwhile results. However, the reaction under study may be controlled by vapour phase diffusion.

p-DAB and O-Nitroaniline were purified by sublimation in vacuo and fractional crystallization with acetone, respectively. Solid state reactions have some novel feature which distinguish them from reactions in solution. These reactions are free from the complicating influence of the solvent and their rates are comparatively slower. They are, therefore, more amenable to kinetic and mechanistic studies and very suitable for the study of weak interactions and for the discovery of new species.²⁻⁵ The development of new technique by Rastogi, et al., has renewed interest in these reactions. They showed that it is easy to follow the progress of a solid-state reaction in a glass capillary if a coloured product is formed.

p-Dimethylaminobenzaldehyde^{6,7} (p-DAB) is a useful chromogenic reagent which gives colour reactions with primary aryl amines, hydrazides of carboxylic acids, pyrrole base, ergot alkaloids, steroid acids, nicotinic acid, antipyrine, novalgine, urea, etc. Qureshi et al.^{8,9} showed that p-DAB can be used for the specific detection of O-Nitroaniline. Unfortunately all these reactions have been studied in only solution. It was therefore, decided to study the Kinetics and mechanism of the solid state reaction of p-DAB with O-Nitroaniline. The reaction in the solid-state was studied in the following way.

PROCEDURE:

A well powdered and thoroughly mixed mixture of p-Dimethylaminobenzaldehyde (p-DAB) and Potassium Hydrogen Sulphate (PHS) in equimolar ratio was used as the reagent (A). A little of the solid was mixed in a micro test-tube with several mg of A. The colour developed at room temperature (25°) as well as on heating was recorded for heating the tube was placed for a few sec in a water-bath preheated to 100°. The limits of identification were determined by starting with known volumes of standard solutions of the compound concerned, evaporating to dryness at 100°, and mixing the solid residue with A.

EXPERIMENTAL:

Clean thick glass capillaries (1-mm bore) with uniform diameters (internal 3 mm and external 9 mm) were taken. Finally

ground was part filled with A by continuous tapping and then the solid test material was added from the other side in similar manner and the position of the interface was noted. The capillaries were sealed from either side with a paste which hardened after some time.

These capillaries were kept in air thermostates maintained at suitable temperature but below the eutectic temperature. The temperature fluctuations were of the order of $\pm 1^\circ$. The start of the reaction was indicated by a change in colour at (p-DAB+PHS) (A-O-Nitroaniline boundary. The distance through which the boundary moved was noted at different time intervals (figure 3.1 and figure 3.2). It also was observed that O-Nitroaniline did not diffuse through product layer where as (A) did. This is schematically shown below.

p-DAB+PHS	AB	O-Nitroaniline
(A)		(B)

In the case it appears that the phase boundary processes are so rapid that equilibrium is established at the boundaries during the entire course of reaction. The diffusion in the product layer is alone rate determining as happens in the case of tarnishing reactions so that if ζ is the thickness of the diffusion layer¹¹

$$\zeta^2 = kt \quad (1)$$

where K is a certain constant and t is the time. Modification has been made in the above relationship to account for the heating

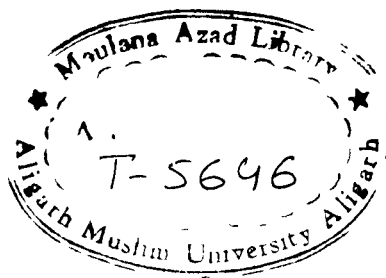
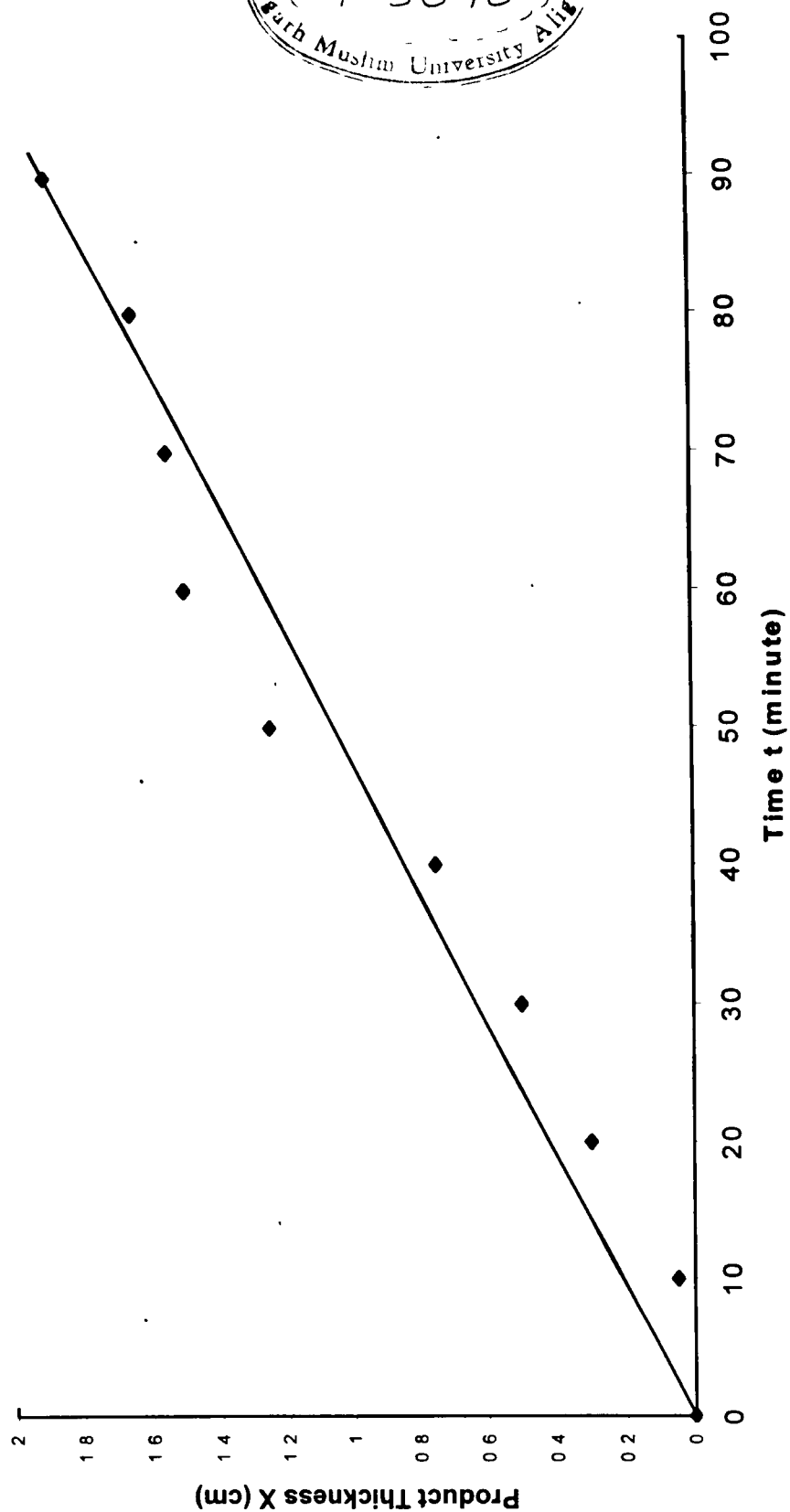


Fig. 3.1 Plot of product thickness verses time for the solid state reaction between (p-DAB+PHS)-O-Nitroaniline at the temperature 20°C.

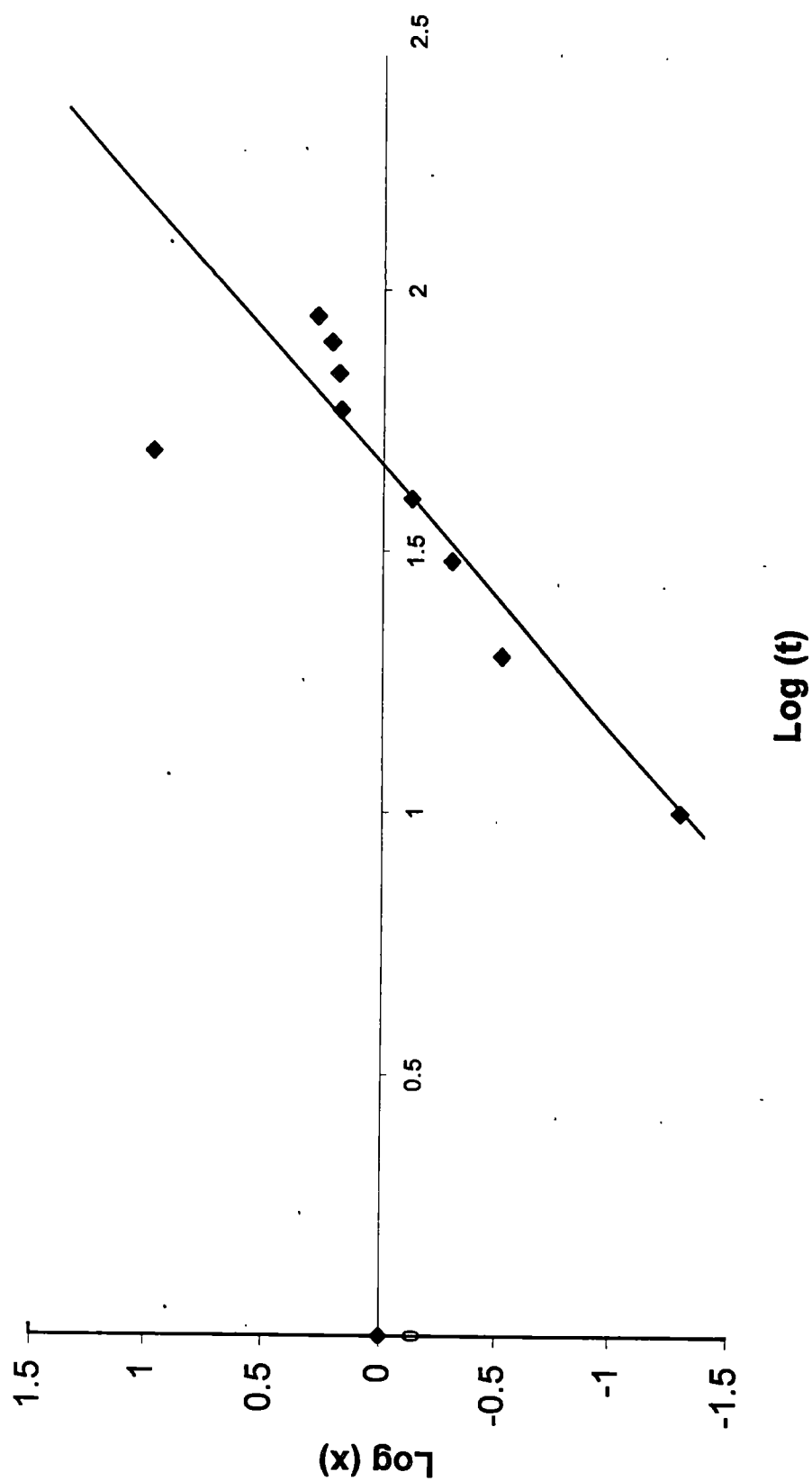


Fig. 3.2 Log of product thickness verses Log of time for the solid state reaction between (p-DAB+PHS)-O-Nitroaniline at the temperature 20°C.

at the interface due to poor thermal conductivities of the solids. For such a case it has been shown that:

$$\zeta^2 = 2k_i t \exp(-P\zeta) \quad (2)$$

where,

$$k_i = C \exp(-E/RT_{\max})$$

C = Certain constant

E = Energy of activation

P = Proportionality Constant

T_{\max} = maximum temperature attained instantaneously in the mixture

In this derivation it is assumed that $T_i - T = K'\zeta$

where K' is another constant so that $P = K'E/RT_i T$; T_i is initial temperature and T is any temperature intermediate between T_i and T_{\max} . Equation (1) did not satisfy the data. For testing equation (2) $\log \zeta/t$ was plotted against ζ straight lines were obtained at all temperatures of observations, justifying the validity of equation (2). This is shown in figure 3.3.

It is interesting to note that all the curves have approximately the same slope, indicating thereby that P has the same value, which should be the case.

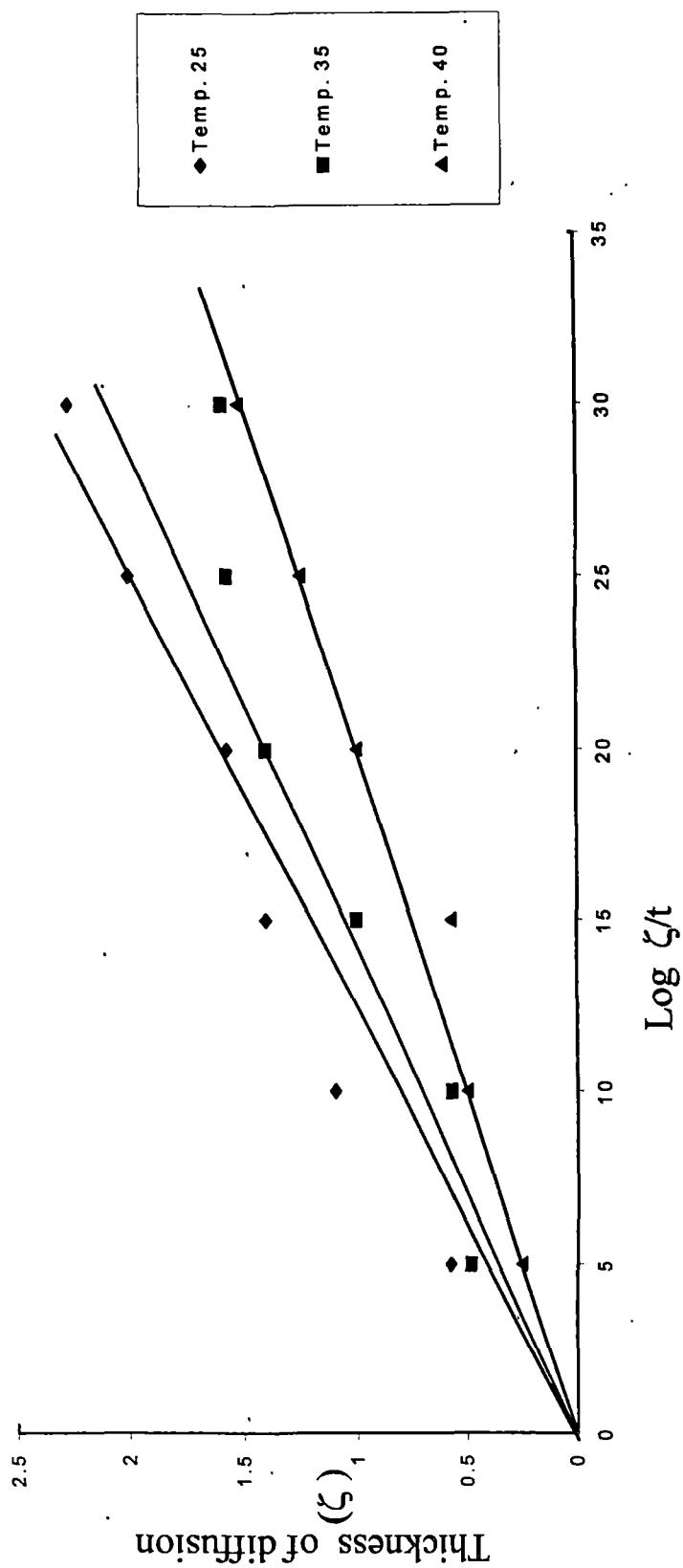


Fig. 3.3 Plot of thickness of diffusion layer (z) versus $\text{Log } z/t$ (time) at different temperature for the solid-state reaction in between (p-DAB+PHS)-O-Nitroaniline.

O-Nitroaniline was AR grade from Fluka and *p*-Dimethylaminobenzaldehyde (*p*-DAB) was Lamba Chemica Ltd. India. Both O-Nitroaniline and *p*-DAB (with PHS), were used as received. Acetone was (Ranbaxy Pvt. Ltd. India) used as solvent in the solution studies. UV-visible spectrophotometer FT-IR spectra were recorded on 1000 systronic spectrophotometer. The association constant were evaluated under the condition that the donor concentration was kept in far excess over the acceptor concentration.

RESULT AND DISCUSSION:

Since O-Nitroaniline absorb strongly in the region of interest the spectra were recorded by taking an equal concentration of the O-Nitroanilines both in the reference and the sample cell. Figure 3.4 gives the charge-transfer spectra for the various O-Nitroaniline-*p*-DAB complexes. As expected for weak molecular complexes they are broad featureless bands.

Figure 3.5 shows the expected dependence of U_{ct} on electron affinity. The electron affinity of ortho, para and m-nitroaniline are known. A plot of electron affinity of these nitroanilines against U_{ct} gives a straight line.

A compensation procedure first proposed by Mulliken¹⁰ may produces an optically silent detector. Therefore, charge-transfer (CT) bands alone may not establish charge-transfer (CT) in these systems but may here to be complemented with an independent data

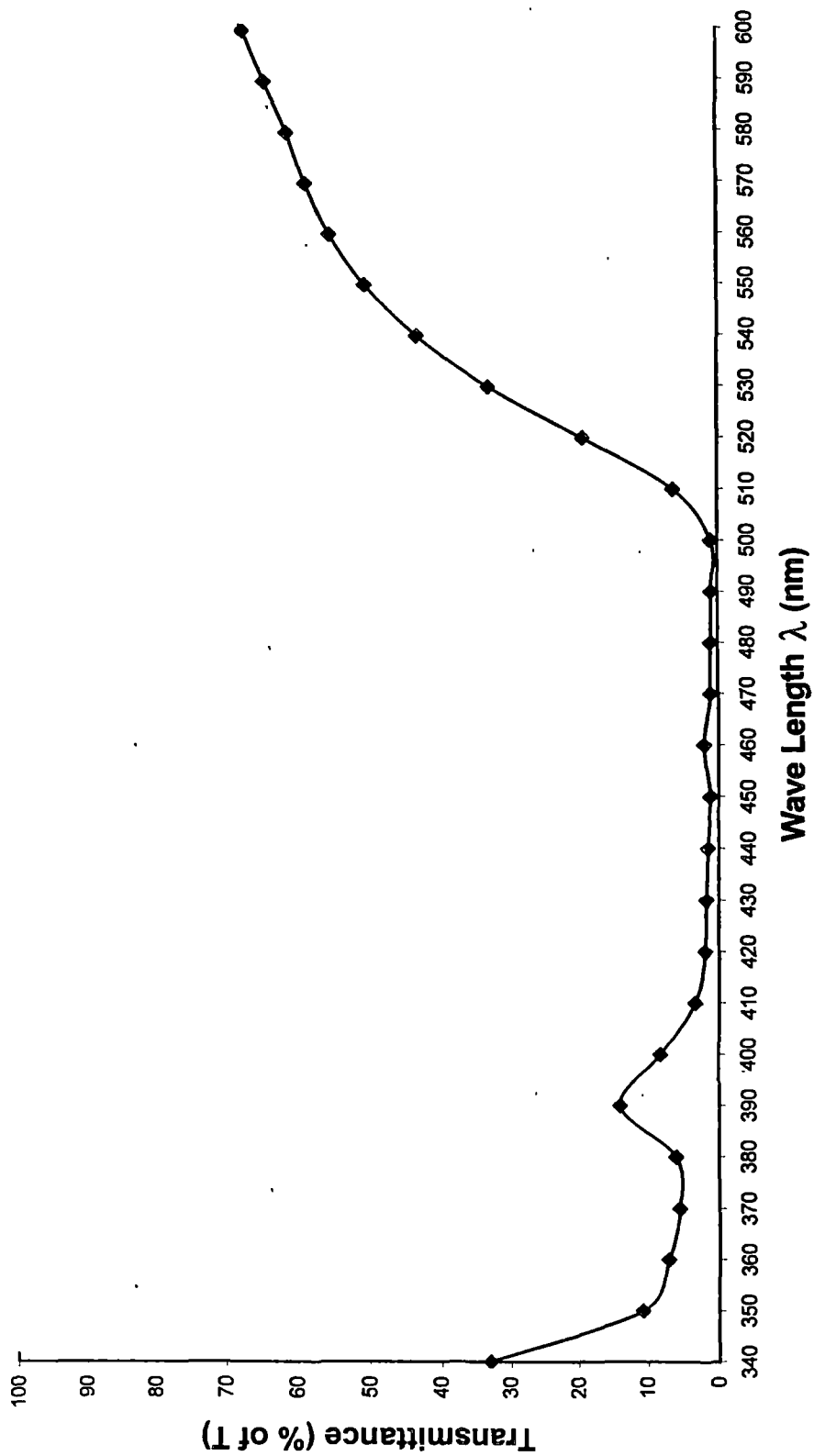


Fig. 3.4 Plot of transmittance verses wavelength (nm) for the solid state reaction between p-DAB-O-Nitroaniline in acetone. λ_{max} found at 390.

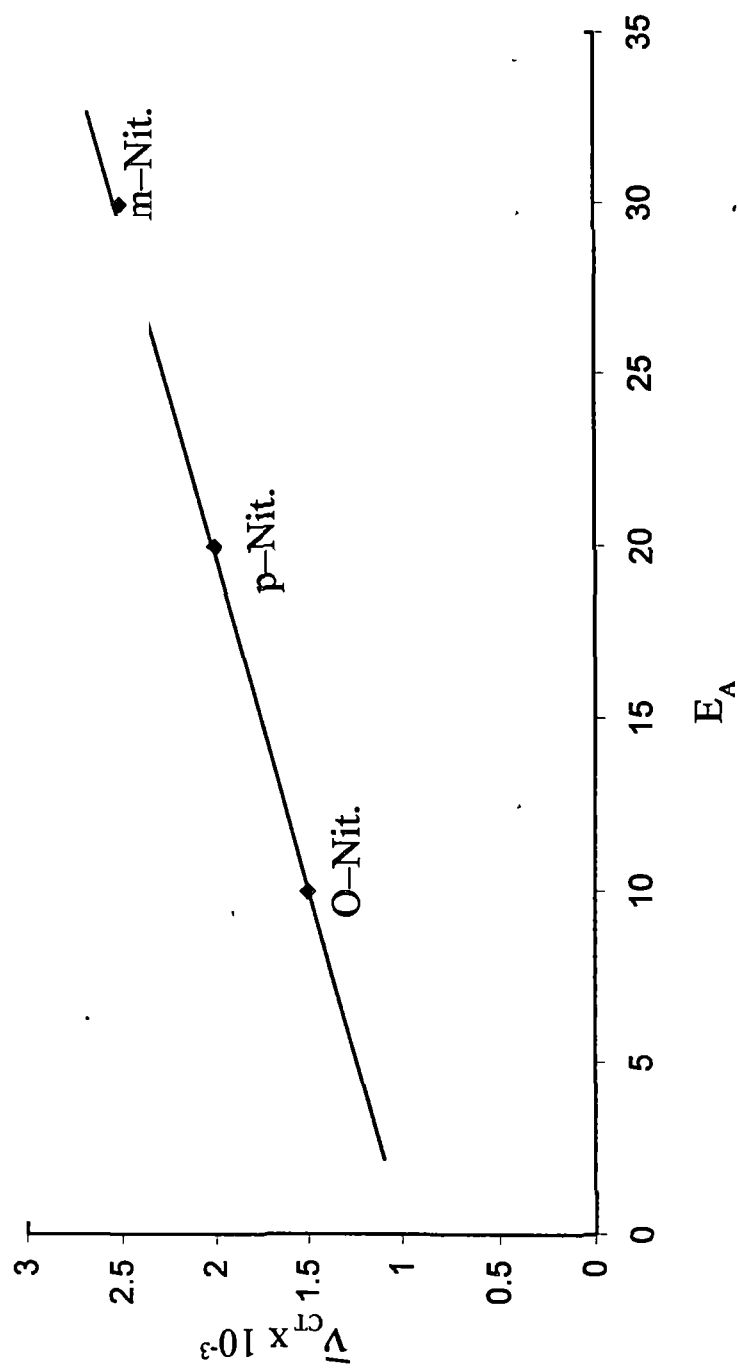


Fig. 3.5 Plot of Electron affinity of O-, p- and m-Nitroanilines verses \bar{V}_{CT} gives straight lines.

we have already shown previous figure 3.5 that there is a linear relation between ν_{CT} electron affinities of those acceptors.

Equilibrium constant measurements were carried out at 390 nm where the polynitroaromatics do not absorb and the above difficulties do not therefore, arise. The equation used was, the well known Benesi- Hildebrand equation

$$\frac{[A]_0}{A} = \frac{1}{K\epsilon_{390}} + \frac{1}{[D]_0} + \frac{1}{\epsilon_{390}} \quad (3)$$

Under the condition $[D]_0 \gg [A]_0$. $[D]_0$ in equation (3) signifies the initial concentration of donor (p-DAB). $[A]_0$ as initial concentration of acceptor (O-Nitroaniline) and A is absorbance of the complex. $[A]_0$ was fixed constant (0.01M) in all solutions while $[D]_0$ was varied (0.1, 0.2, 0.3 0.4 M ...). A plot of $[A]_0/A$ vs $1/[D]_0$ is linear with the slope equal to $1/K\epsilon_{390}$ and intercept $1/\epsilon_{390}$. The association constant K is then obtained by dividing the intercept by the slope. After this process we started the work with the help of Job's method. The ratio of compound as (1 ml Compound.+9 ml acetone to 9 ml compound +1 ml acetone) at the wavelength at 390 (constant). The % of transmittance shown in figure 3.6. The λ_{max} at 390 the peak maxima at the ratio (9:1). Now at the constant λ_{max} (390) in the process of Job's method the ratio 9:1 occurs maxima 38.1 (% of T).

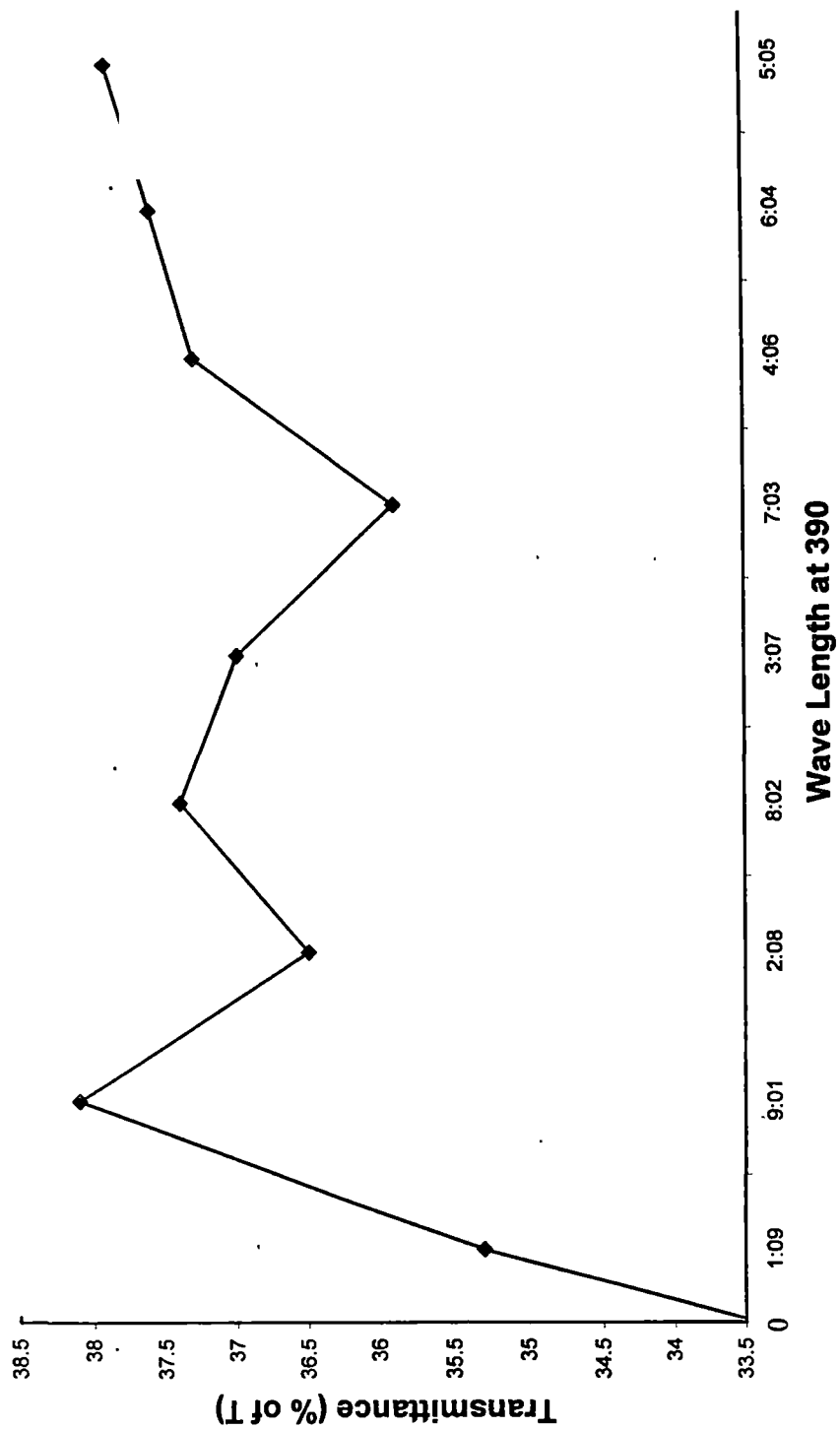


Fig. 3.6 Plot of transmittance verses wavelength at 390 (nm) (Job's method maxima at 9:1 ratio).

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CHAPTER - IV

**MULTIPLE CHARGE-TRANSFER BANDS IN THE
REACTION OF p-NITROPHENOL (p-NTP) AND
p-DIMETHYLAMINO BENZALDEHYDE (p-DAB)**

INTRODUCTION:

The existence of molecular complexes between nitro-substituted benzenes and aromatic hydrocarbons has long been recognized. Many theories have been advanced to explain the nature of these complexes but only recently has one been purposed which is completely acceptable. This theory is found in a series of papers by Mulliken¹ whose general quantum mechanical-treatment of molecular complexes encompassed all of the preceding major, classical theories.² Mulliken suggested that the formation of molecular complexes from two aromatic molecules can arise from the transfer of an electron from a π -molecular orbital of a lewis acid, with resonance between this dative structure and the no-bond structure stabilizing the complex. He also noted the possibility of complex formation through the donation of an electron from a non-bonding molecular orbital in a lewis base to a vacant π -orbital of an acceptor (n- π interaction)^{1b}, with resonance stabilization of the combination.

Mulliken's ideas have been supported by spectroscopic evidence. The dichroism studies by Nakamoto³ of molecular complexes of a type similar to those treated in this paper clearly indicate the existence of charge-transfer forces operating between the two components of the complex. The original attraction of the two components, according to Nakamoto, arose from mutual polarizing

forces which caused attracting dipoles. When the two molecules approached each other closely enough so as to be in the effective π -electron fields of each other, the electron transfer could then occur.

The intermolecular charge-transfer predicted by Mulliken gives rise to intense electronic absorption bands in many complexes. These bands were examined by McConnell, et al.,⁴ and Hastings, et al.,⁵ who used them to set up empirical methods which would predict the wave lengths and intensities of these charge-transfer absorptions.

Where as the ultraviolet region can be used to study the electronic characteristics of these complexes, the infra-red spectra can be utilized to examine the result of the charge-transfers. Since the stability of these complexes arises from a shift of electron density from the donor to the electron deficient acceptor molecule, the infra-red region should record the effect of the change of electron density in the components upon the vibrations of the atoms within the individual molecules. Study of vibrational spectra may also reveal which parts of the molecules play an active role in complex formation.

Charge-transfer complexes of organometallic donor have been studied extensively. Some of these studies⁶⁻¹⁰ the importance of these complexes. Though complexes with alkali donors have been

studied extensively their nitro counter parts have been much less studied. In the present study it is shown that p-Dimethylaminobenzaldehyde forms a molecular complex with p-Nitrophenol in both solid and solution. This complex shows a multiple charge-transfer (CT) spectrum centered at 370 and 430 nm. IR studies have been carried out and equilibrium constant has been measured. Preliminary solid-state studies by Rastogi capillary technique¹¹ (figure 4.1) has also been carried out.

EXPERIMENTAL:

p-Nitrophenol (p-NTP) was AR Grade from Fluka and p-Dimethylaminobenzaldehyde (p-DAB) was Lamba Chemica Ltd. India. Both p-Nitrophenol and p-Dimethylaminobenzaldehyde were used as received. Acetone (Ranbaxy India Ltd.) was used as solvent in the solution studies. UV-visible studies were carried out on systronic 1000 spectrophotometer. FT-IR were recorded on Nicolet 5Dx FT-IR spectrophotometer.

RESULT AND DISCUSSION:

A spectrophotometer UV-visible spectrum of p-Nitrophenol in acetone shown a broad featurless band centered at 370 nm while that of p-Dimethylaminobenzaldehyde shows an absorption maxima at 390 nm. p-Nitrophenol and p-Dimethylaminobenzaldehyde form a yellow coloured charge-transfer complex in acetone. The complex of p-Nitrophenol and p-Dimethylaminobenzaldehyde was prepared by

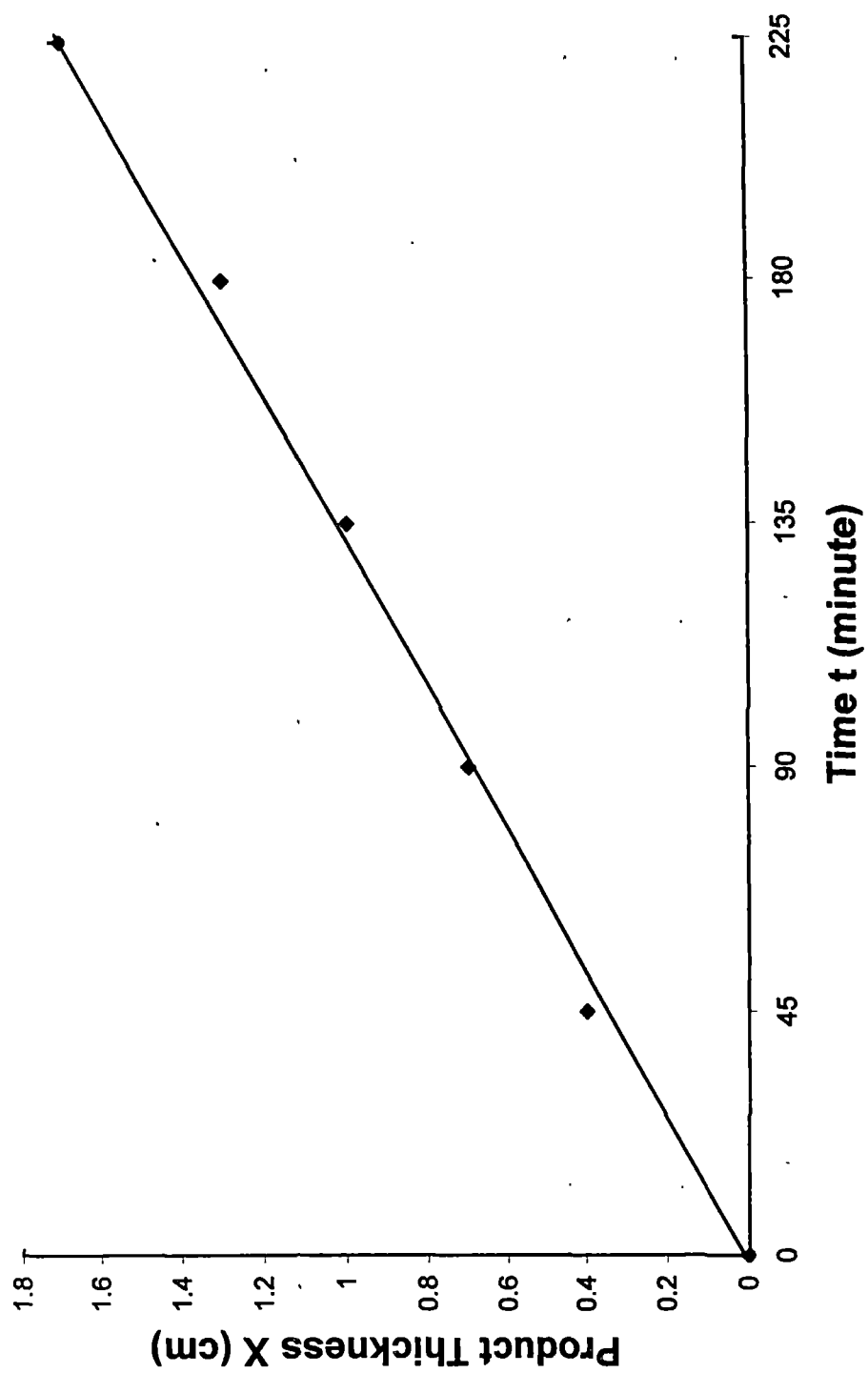


Fig. 4.1 Plot of product thickness verses time for the solid state reaction between p-DAB+p-Nitrophenol at the temperature 35°C.

mixing equal volumes of 0.1M each solution in acetone. The UV-visible spectrum was recorded after taking an equal concentration of p-Nitrophenol in the reference cell. This was done to compensate for the small absorption of p-Nitrophenol in the region of charge-transfer (CT) bands. This procedure follows a method developed by Mulliken.¹² Two bands appeared in the spectrum of the complex (figure 4.2). These are centred at 370 nm and 430 nm. Therefore, p-Nitrophenol and p-Dimethylaminobenzaldehyde complex is a case of multiple charge-transfer (CT) complex. The multiplicity may arise from electron donation from more than one energy level in the donor to more than one energy level in the acceptor.¹³ According to McGlynn two isomeric complexes are formed if the maxima overlap principle is applied.¹⁴ Figure 4.2 shows the two charge-transfer bands of the NTP-DAB complex.

FT-IR studies were carried out in solution and by Nujol disk method as well. In Nujol disk method equimolar quantities of finely powdered p-Nitrophenol and p-DAB were mixed and the reaction initiated in a oven controlled at a temperature 309k, a yellow coloured complex resulted which was then mixed with Nujol. After a systematic study of 40 molecular complexes with picric acid kross¹⁰ has postulated certain regularities in the IR spectra of acceptor molecule. According to kross only the NO₂ asymmetric stretching vibrations showed significant changes. Assuming that the

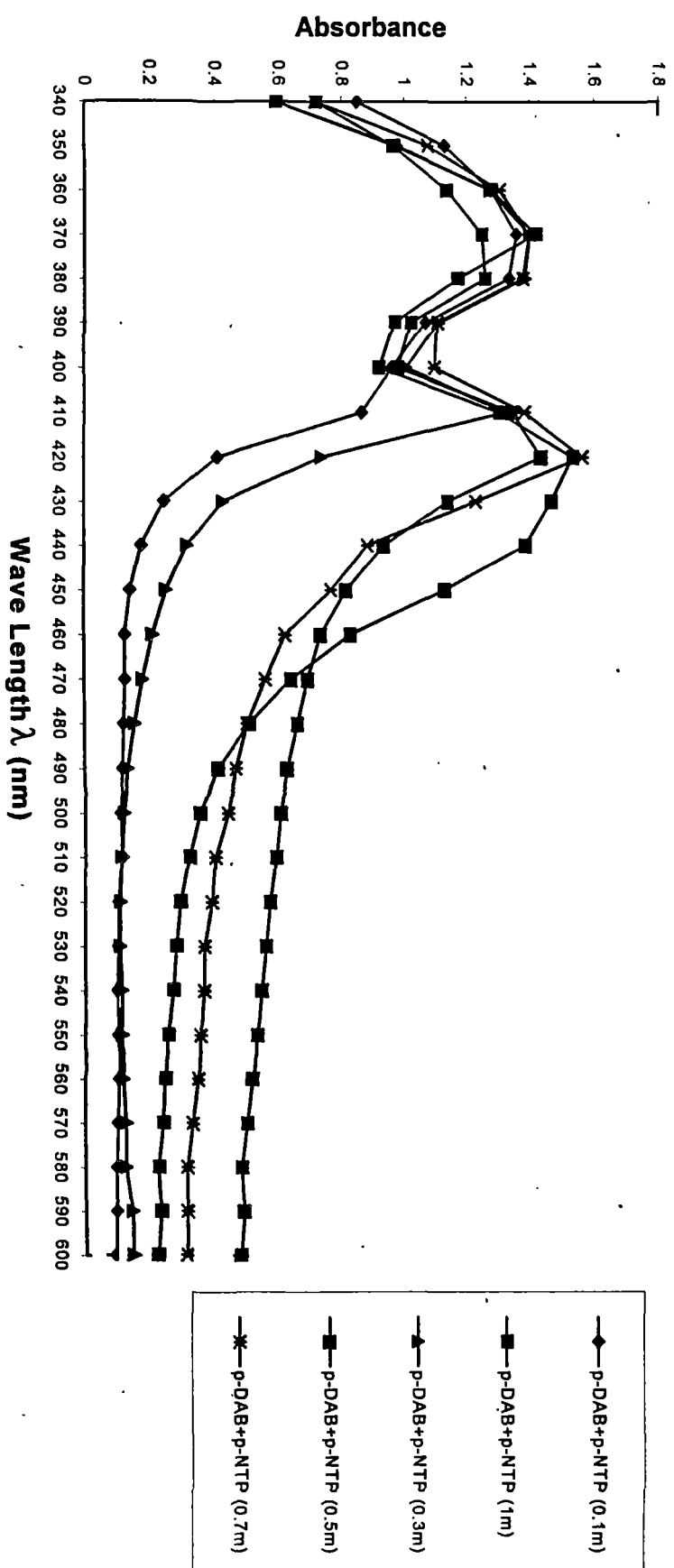


Fig. 4.2 Multiple charge-transfer bands of the p-Nitrophenol-p-DAB complex.
 $\lambda_{\text{max}}=370$ and 420 (nm)

NO_2 group of nitrophenol behaves similar to the NO_2 group of picric acid, it is possible to interpret the IR spectrum of the NTP-DAB complex (figure 4.3) on the basis of the studies of Kross. p-Nitrophenol shows a broad band centred at 1600 cm^{-1} and another at 1500 cm^{-1} due to nitro asymmetric stretching vibrations. In the complex, while the 1500 cm^{-1} band remains without shift, the broad band localized at 1600 cm^{-1} shifts to 1610 cm^{-1} . A shift of 10 cm^{-1} shows a weak interaction. As per Kross classification these features there is a localized intermolecular interaction could be due to the p-orbitals of the p-Nitrophenol and π -orbitals of the benzene ring of p-Dimethylaminobenzaldehyde. The localized intermolecular interaction is probably due to the contribution of the metal to the complex.

After surveying the IR spectra of several related organometallic compounds, one comes to the conclusion that the metal c-bands like some are close to 1330 cm^{-1} . I therefore ascribe the band at 1370 cm^{-1} in free p-Nitrophenol to Sb attached to a phenyl ring. A band in this position is not present in the spectrum of p-Nitrophenol. In complex this peak shifts to 1380 cm^{-1} again showing a shift of 10 cm^{-1} (towards lower frequency) as in the case of nitro asymmetric stretching band. As mentioned a shift of 10 cm^{-1} shows a weak charge-transfer (CT) complexation. In solution again the nitro asymmetric absorption shows a shift of 10 cm^{-1} to lower frequencies.

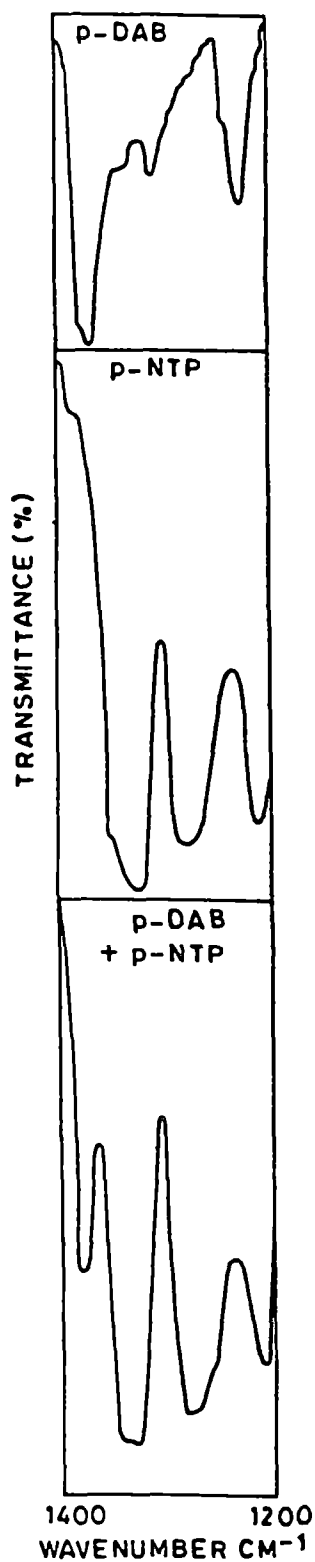


Fig. 4.3: IR Spectra shows that a shift of 10 cm⁻¹ from 1370 cm⁻¹ to 1380 cm⁻¹.

The solid-state reaction between p-Nitrophenol and p-Dimethylaminobenzaldehyde was carried out by placing well powdered samples with uniform particle sizes in a glass capillary from either end and till they meet at junction. The capillary was placed in an oven controlled at a temperature 40° . A yellow colour developed at the boundary of p-Nitrophenol and p-Dimethylaminobenzaldehyde and moved toward p-Nitrophenol showing that p-Dimethylaminobenzaldehyde diffuses into p-Nitrophenol in the solid-state reaction. The movement of coloured boundary in p-Nitrophenol was recorded as a function of time (figure 4.1). The kinetic plot is given in figure 4.4. The rate equation followed as:

$$\lg \epsilon = 3.125 \log t - 1.8$$

Association constants K were evaluated by the method of Foster¹⁶ under the condition $[A]_0 = [D]_0$ and applying the equation.

$$\frac{[A]_0}{A} = \frac{1}{K\epsilon_{\lambda}} \frac{1}{[D]_0} + \frac{2}{\epsilon_{\lambda}}$$

Where $[A]_0$ is the initial concentration of acceptor equal to $[D]_0$, the initial concentration of the donor. A is the absorbance of the complex at λ , K is the association constant and ϵ_{λ} is the molar absorptivity of the complex at λ . On plotting $[A]_0/A$ vs $1/[D]_0$ for a series of solutions a straight line is obtained under the condition $[A]_0 = [D]_0$ with the slope equal to $1/K\epsilon_{\lambda}$ and the intercept equal to

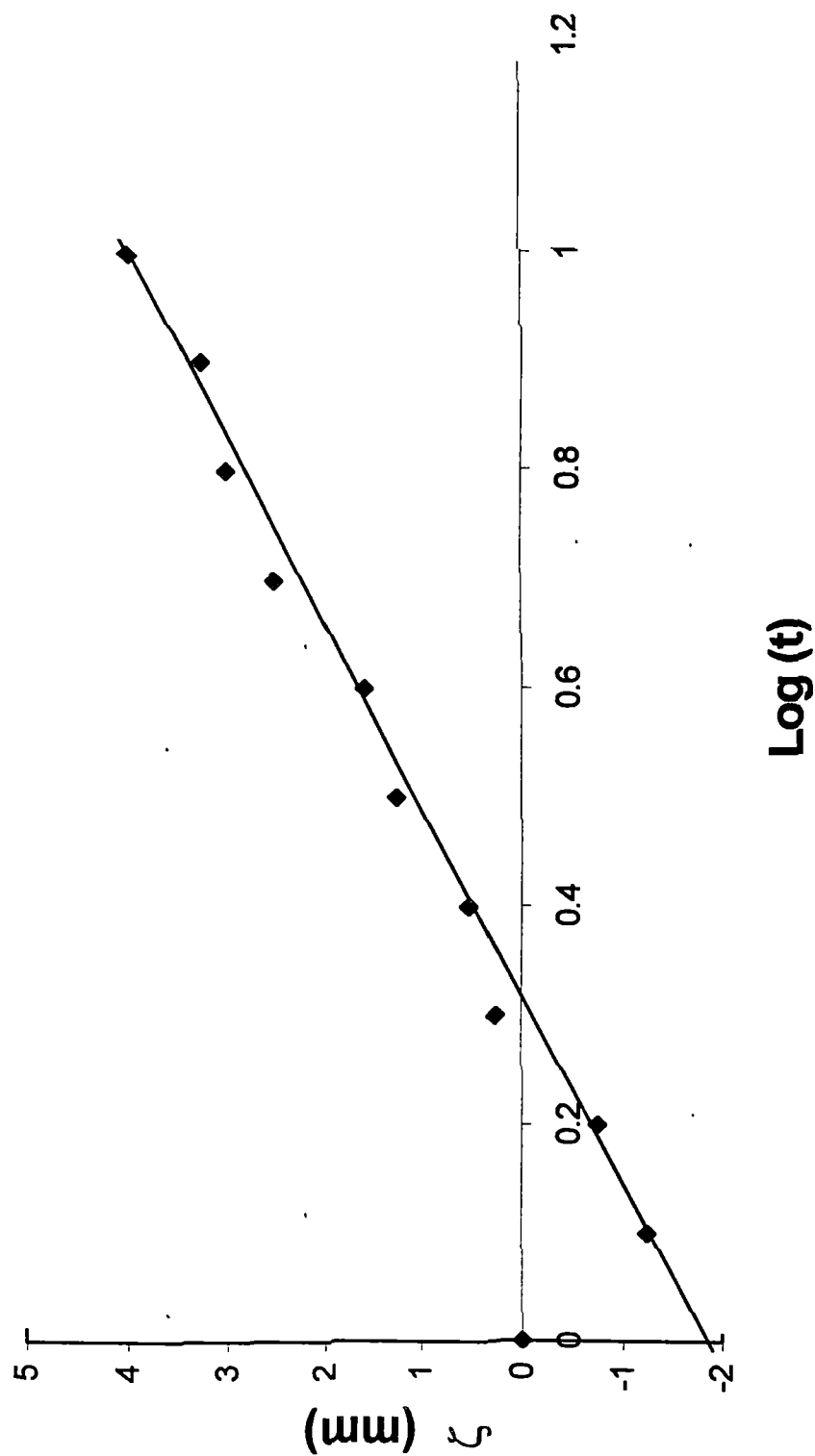


Fig. 4.4 Plot of product thickness ζ (nm) verses Log of time for the solid state reaction between p-DAB+p-Nitrophenol.

$2/\epsilon_{\lambda}$ (figure 4.5). This study was carried out at 420 nm with the concentrations ranging from 1 m to 0.7m (1m, 0.1m, 0.3m, 0.5 m and 0.7m).

In conclusion one can say that p-Nitrophenol and p-Dimethylaminobenzaldehyde form a yellow coloured weak charge-transfer complex in acetone as well as solid-state. It is a case of multiple charge-transfer complex; the two charge-transfer bands being centred at 370nm and 420 nm. UV-visible spectral studies also shows that the products of the reaction between p-Nitrophenol and p-Dimethylaminobenzaldehyde in the solid-state and the solution are the same. The IR studies suggest that there is an interaction between Sb p-Nitrophenol and p-Dimethylaminobenzaldehyde besides the π - π^* interaction between the π -orbitals of p-Nitrophenol and p orbitals of the benzene ring of p-Dimethylaminobenzaldehyde.

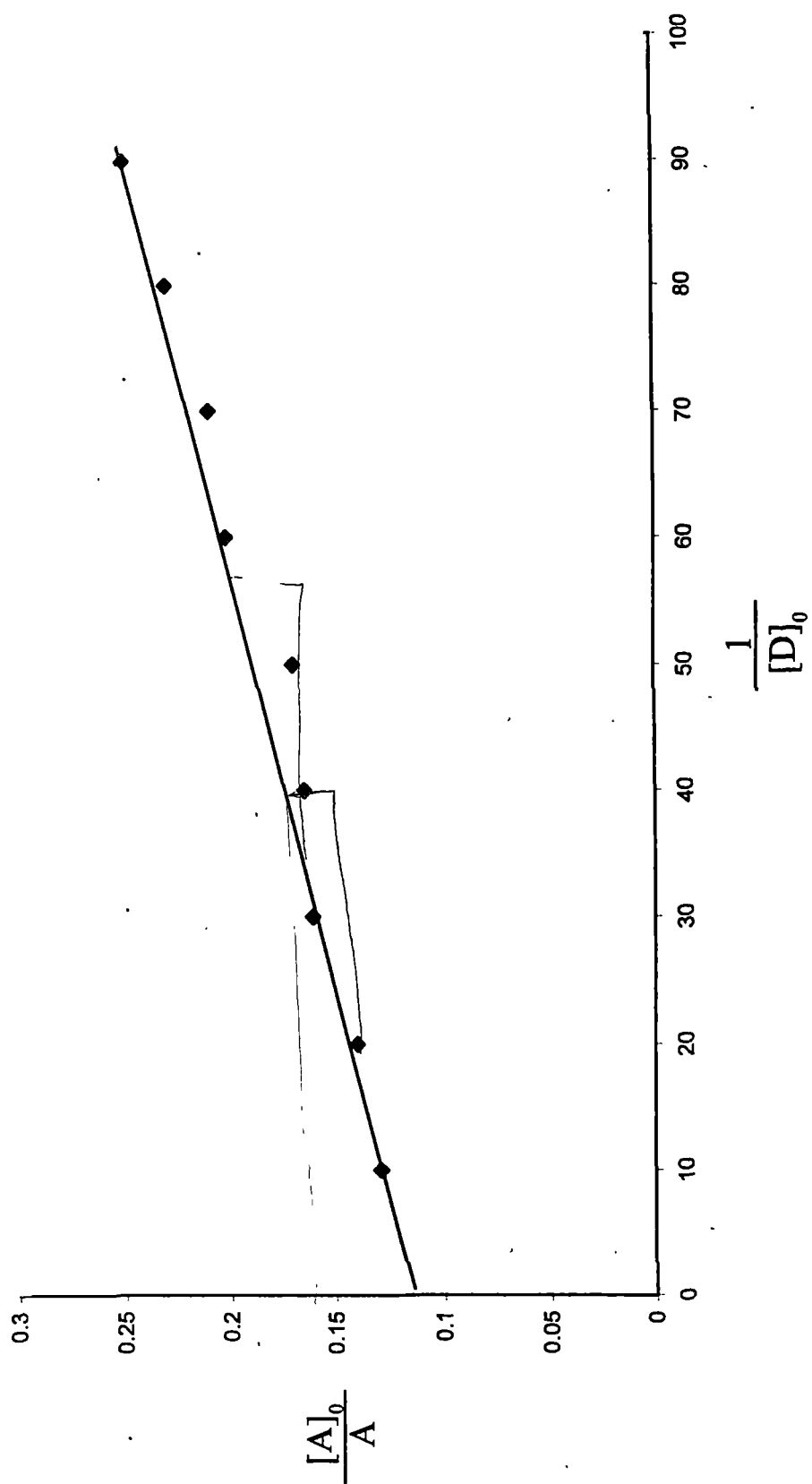


Fig. 4.5 Foster's plot for the evaluation of the association constant of the p-Nitrophenol-p-DAB complex at wave length 420 (nm).

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CHAPTER - V

**SPECTROPHOTOMETRIC METHOD FOR THE
DETERMINATION OF THE FORMULA OF THE
COMPLEX. REACTION BETWEEN 3,5-DINITRO
BENZOIC ACID AND p-DIMETHYLAMINO
BENZALDEHYDE**

INTRODUCTION:

The organic solid-state reactions resulting in the formation of charge-transfer complexes are of current interest owing to their utility in the study of organic metals^{1,2} in photographic processes and in energy conversion system.³ These reactions find applications in stereospecific synthesis⁴ and in electronic and electro- static devices.³ Although weak charge-transfer complexes are not involved, nevertheless, they may reflect the mechanism of these devices.

The present work was undertaken to study the kinetics and mechanism of reaction between 3-5- Dinitrobenzoicacid (DNBA) and p-Dimethylaminobenzaldehyde (p-DAB) in solid state. It has been observed that the colour of the products did not show any change even when the reacting species were mixed in different molar ratios. Infra-red and spectrophotometric studies were used to investigate the formation of a charge-transfer complex.

EXPERIMENTAL:

3,5- Dinitrobenzoicacid (DNBA) was GR reagent from E.Merck (Darmsdadt) and p-Dimethylaminobenzaldehyde (p-DAB) was BDH Anala R BDH Poole. England and were used as received. Acetone was an AR reagent. Triple distilled conductivity water was used throughout. In spectrophotometric method, all measurements were carried out on systronics 118 UV-Vis spectrophotometer at 25°C.

For the measurements of K , 3 mls of 3,5-Dinitrobenzoic acid (DNBA) solution of requisite concentration were taken in tube in which 1 ml increments of p-DAB under the conditions $[p\text{-DAB}] \gg [3,5\text{-DNBA}]$ were added and absorbance recorded at 420nm (λ_{max}). References for 3,5-Dinitrobenzoicacid (DNBA) were prepared in a like manner. The equation used for the measurement of K , takes the form.⁸

$$\frac{[D]_0[A]_0}{A} = \frac{[D]_0}{\epsilon_\lambda} + \frac{1}{K\epsilon_\lambda}$$

If a plot is made of $[D]_0 [A]_0/A$ Vs. $[D]_0$, a straight line is obtained with slope $1/\epsilon_\lambda$ and the intercept $1/K\epsilon_\lambda$. The charge-transfer complexes of 3,5-Dinitrobenzoicacid (DNBA) have been studied largely as the 3,5-Dinitrobenzoate ion in aqueous media.⁹ This is perhaps the first study showing the charge-transfer (CT) complex formation of 3,5-Dinitrobenzoicacid (DNBA) in non-aqueous or aqueous mixed media.

RESULTS AND DISCUSSION:

Initially the reaction between 3,5-Dinitrobenzoicacid (DNBA) and p-DAB was studied in pure acetone. Figure (5.1) shows the charge-transfer (CT) band of this system. The method of Mulliken¹⁰ was used to isolate this band where by an equimolar

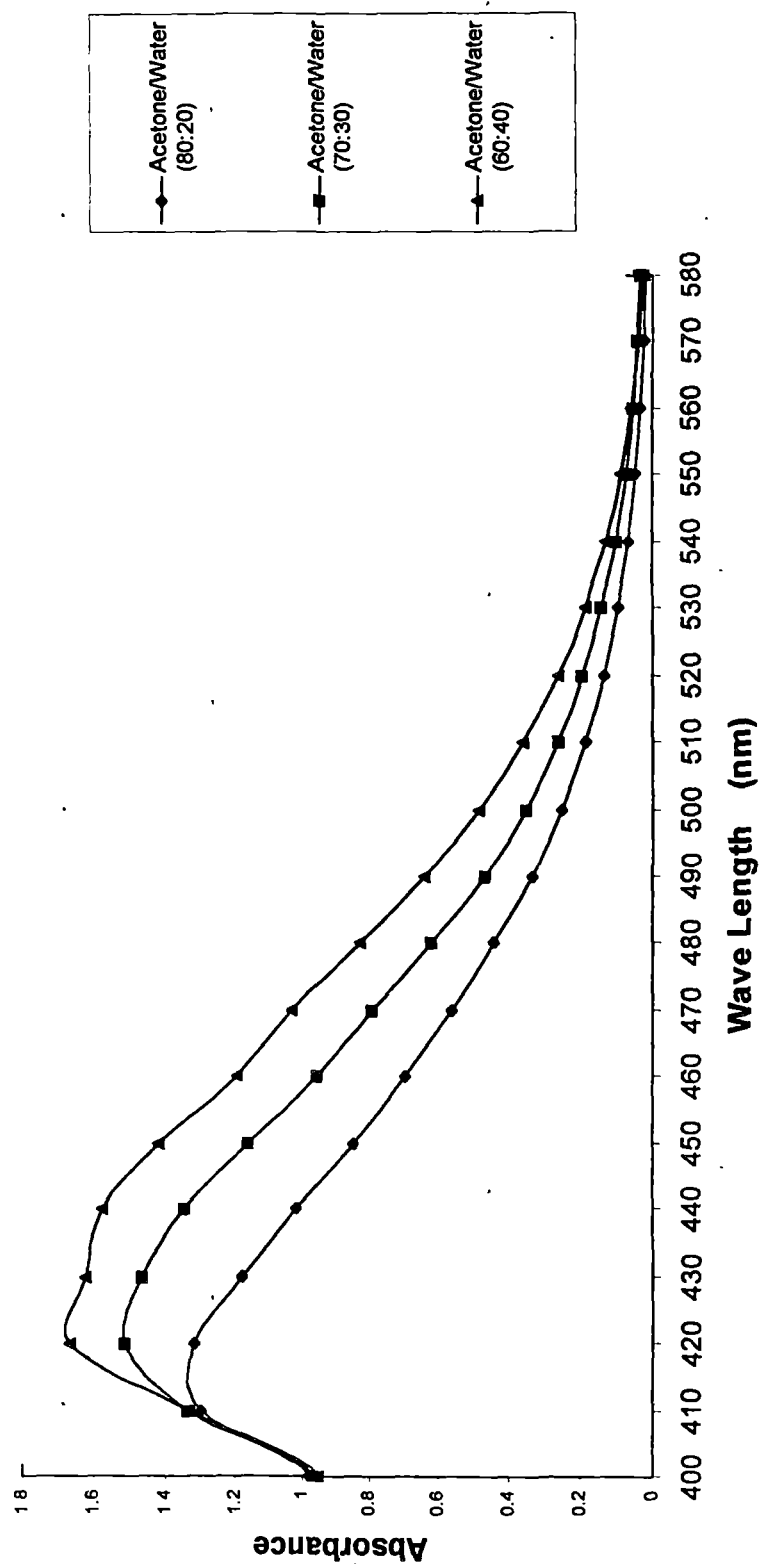


Fig. 5.1 Absorption spectrum of the 3,5-Dinitrobenzoic acid-p-DAB charge-transfer system in Acetone/water. $\lambda_{\max} = 420$ nm.

amount of 3,5-Dinitrobenzoicacid (DNBA) (which absorbs in the region of interest) was taken in the reference cell. p-DAB did not absorb in the region of interest.

It was seen that excess solvent destabilizes the complex. Therefore, the association constant K was measured in a single tube having a known fixed amount of 3,5-Dinitrobenzoicacid (DNBA) initially and to this solution was continuously added fixed increments of a solution of p-DAB and the absorbances measured. Here the concentration of both reagents changes continuously. Different blanks were prepared for different concentrations of 3,5-Dinitrobenzoicacid (DNBA).

The association constant in acetone was evaluated by the scott equation⁸ which is a variant of the Benesi- Hildebrand equation¹¹ and is often the preferable method¹² (figure 5.2). The association constant and ϵ_{\max} values are tabulated in table 1. It is seen that though K is in the range observed (e.g. 23.6 for the N-(Indole-3-acryloyl) imidazole-3,5-dinitrobenzoate in water) the molar absorptivity is absurdly low. This alongwith the destabilisation of the complex in excess solvent indicated that perhaps electro-static forces are important.

Consequently results in mixed aqueous media were also carried out and are also reported in table 1. It is seen that though in all cases studied the λ_{\max} remains the same, k and ϵ_{\max} change

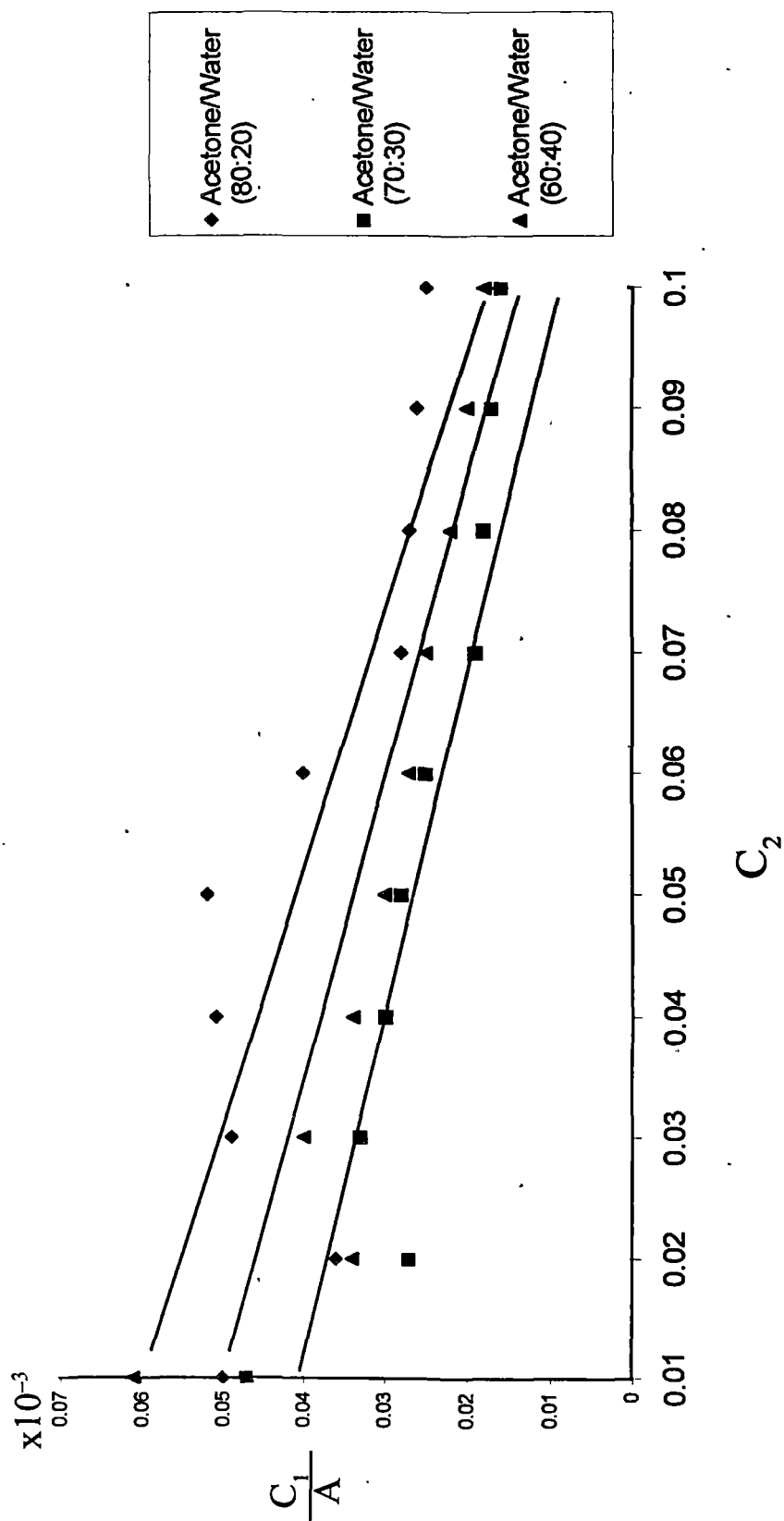


Fig. 5.2 Foster's plot for the evaluation of the association constant of the 3,5-Dinitrobenzoic acid-p-DAB complex.

dramatically. k increases from 25.0, in pure acetone to 625.0 in 60:40 mixture of acetone and water. λ_{\max} does not show any particular trend with K and neither is this expected.¹³ The almost abnormally large increase in k as the water content increases shows that electrostatic effects predominate. Further when in one particular case (80:20, Acetone/Water mixture) the measurements for k were carried out away from λ_{\max} (370 nm) i.e. at 420 nm a large wavelength dependence in k was found (Table 1). This observation confirms the role of electrostatic contributions.

IR spectroscopy is a versatile technique to study solid-state reactions. It has a virtual application to reactions between amorphous solids, especially charge-transfer complexes where it may pin point whether a complex is π - π^* , n - π^* etc.

The acceptors are generally classified as non acidic and acidic compounds. The former type can only form DA complexes involving electron transfer while the acidic compounds are capable of forming both the electron transfer complexes and those comprising proton donation to the donor. Since the stability of these complexes arises from a shift of the electron density from the donor to the electron deficient acceptor molecule, the infra-red region should record the effect of the change of electron density in the components upon the vibrations of the atoms within the individual molecules. Study of vibrational spectra may also reveal which parts

of the molecules play an active role in complex formation. The spectrum of the molecular complex should be a summation of the spectra of the two components. After a systematic study of 40 molecular complexes with the picric acid, Kross has postulated certain regularities in the IR spectra of the acceptor molecule.

Table-1

K and λ_{\max} for the 3,5-Dinitrobenzoic acid and p-Dimethylaminobenzaldehyde charge-transfer system in pure Acetone and mixed aqueous solvents of Acetone.

Solvent	$\lambda_{\max}(\text{nm})$	K	ϵ
Acetone	420	25.0	1.33
Ace/H ₂ O (80:20)	420	30	66.6
Ace/H ₂ O (70:30)	420	290	11.5
Ace/H ₂ O (60:40)	420	625	40

According to Kross only the NO₂ asymmetric stretching vibration and the C-H out of plane bending vibration showed significant changes. Assuming that the NO₂ group of the 3,5-Dinitrobenzoic acid (DNBA) behaves similar to the NO₂ group of

picric acid it is possible to interpret the IR spectrum of the DNBA-p-DAB complex on the basis of the studies of Kross. Just like picric acid 3,5-Dinitrobenzoic acid (DNBA) shows a broad band with a maximum at 1525 cm^{-1} due to the two nitro groups present in the molecule. According to Kross the donors may be divided into 3 groups on the basis of their IR spectrum. In group 1 there are mostly hydrocarbons which show only one $\nu_{\text{as}} \text{NO}_2$ band greater in frequency than that in picric acid. The corresponding $\delta_{\text{C-H}}$ out of plane frequencies are all lower than in picric acid. Such complexes have been classified by Kross as π - π complexes. In group 2 he has included about twelve substances where the hydrocarbon donor contains CH_3 , OCH_3 , OH and NH_2 . In such cases second band appears at a lower frequency while the first band remains at its original position. These compounds are expected to show in addition to π - π^* bonding, a localized intermolecular interaction. In group 3 he has included those substances which show a π - π^* and n - π transition. In this case the spectrum of the complex shows two $\nu_{\text{as}} \text{NO}_2$ vibrations. One stronger than the other. The more intense band is located in the region in which the NO_2 vibration is found in picric acid and the weaker band is found at considerably higher frequencies. The δ_{CH} out of plane vibrations invariably appear at higher frequency than in picric acid. A characteristic common to all of the complexes in this group is that the donor molecule contains an atom which

permits it to act as n-base and forms strong localised $n-\pi$ complexes. The charge-transfer (CT) takes place between non-bonding orbital or the hetrocyclic nitrogen atom and the vacant orbital of one of the nitro groups.

On mixing equimolar amounts of 3,5-Dinitrobenzoicacid (DNBA) and p-DAB and recording the IR spectra a shift of 20cm^{-1} (from 1540cm^{-1} to 1520cm^{-1}) is observed for the $\nu_{\text{as}} \text{NO}_2$ vibration of 3,5-Dinitrobenzoicacid (DNBA) while the band at 1340cm^{-1} in 3,5-Dinitrobenzoicacid (DNBA) shifts to 1370cm^{-1} in the complex showing an over all shift of 30cm^{-1} . These results are in consonance with the studies of kross and Fassel⁷. The trend observed by us indicate as $\pi-\pi^*$ charge-transfer (CT) complex in accordance to the above classification.

CALCULATION:

At 80:20 ===== Ace/ H_2O

$$\begin{aligned}\text{Slope} &= \frac{0.30}{0.02} \times 10^{-3} \\ &= 3/20 = 0.015\end{aligned}$$

$$1/\epsilon_{\text{max}} = 0.015$$

Therefore,

$$\epsilon_{\text{max}} = 66.6$$

$$1/K\epsilon = 0.5 \times 10^{-3}$$

$$\begin{aligned}
 K\epsilon &= 1/0.5 \times 10^{-3} \\
 &= 2 \times 10^{-3} = 2 \times 10^{-3}
 \end{aligned}$$

$$K = \frac{2}{66.6} \times 10^{-3}$$

$$K = \frac{2000}{66.6} = 30$$

$$K = 30 \quad \epsilon = 66.6$$

Similarly for 70:30 and 60:40

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